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for May, 1936

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Acetic Acid Glacial
Acetic Acid Pure
Acetic Acid Redistilled
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Alum—Filter
Alum—Paper Makers
Alum—Pearl
Alum—Potash U.S.P.
Aluminum Sulphate Commercial and Iron Free
Aluminum Chloride Crystals
Aluminum Chloride Solution
Ammonium Nitrate
Ammonium Nitrate, C. P.
Ammonium Sulphate 99.5%
Aqua Ammonia
Aqua Fortis
Arsenic Acid
Barium Carbonate
Barium Chloride
Barium Sulphate—(Blanc Fixe)
Battery Acid
Battery Coppers
Battery Zinc
Bi-Chromate of Soda
Bi-Chromate of Potash
Bi-Sulphate of Soda
Bi-Sulphite of Soda Solution
Bright Zinc
C. P. Ammonium Hydroxide
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Cadalyte Bright Dip
Cadmium
Cadmium Anodes
Cadmium Hydrate
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Cadmium Sulphide
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Calcium Phosphate, Tribasic
Chromic Acid
Delimer K*
Duclean—Iron drum cleaner
2 Ethyl Hexenal
Fire Retardants
Fixtan A & B
Formic Acid
G. B. S. Soda
Glauber's Salt
Glauber's Salt Anhydrous
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Nogas
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Potassium Silicate Solution
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Salt Cake
Sherardizing Zinc
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Sodium Pyrophosphate
Sodium Formate
Sodium—Lead Alloy
Sodium—Zinc Alloy
Sodium Silico Fluoride
Soldering Flux Crystals
Soldering Flux Solution
Stab Zinc
Strontium Carbonate
Strontium Nitrate
Sulphate of Soda Anhydrous
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Sulphide of Soda Fused Solid
Sulphite of Soda Crystal
Sulphuric Acid
Super Sulphate of Soda
Thallium Sulphate
Titanyl Sulphate
Tin Crystals
Tinning Flux
Tri-Sodium Phosphate
Zinc Anodes
Zinc Chloride Fused
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Zinc Chloride Solution
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Zinc Intermediate
Zinc Oxide
Tomahawk* 35% Leaded
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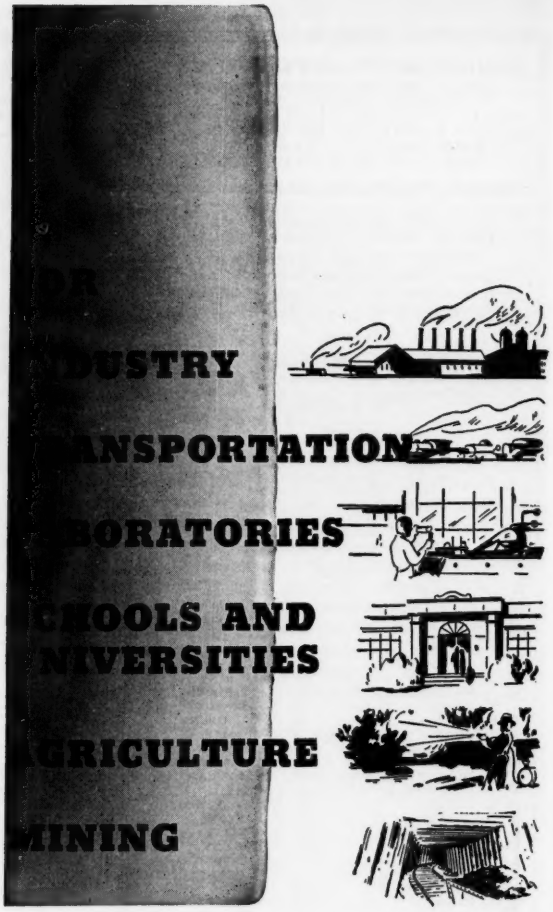

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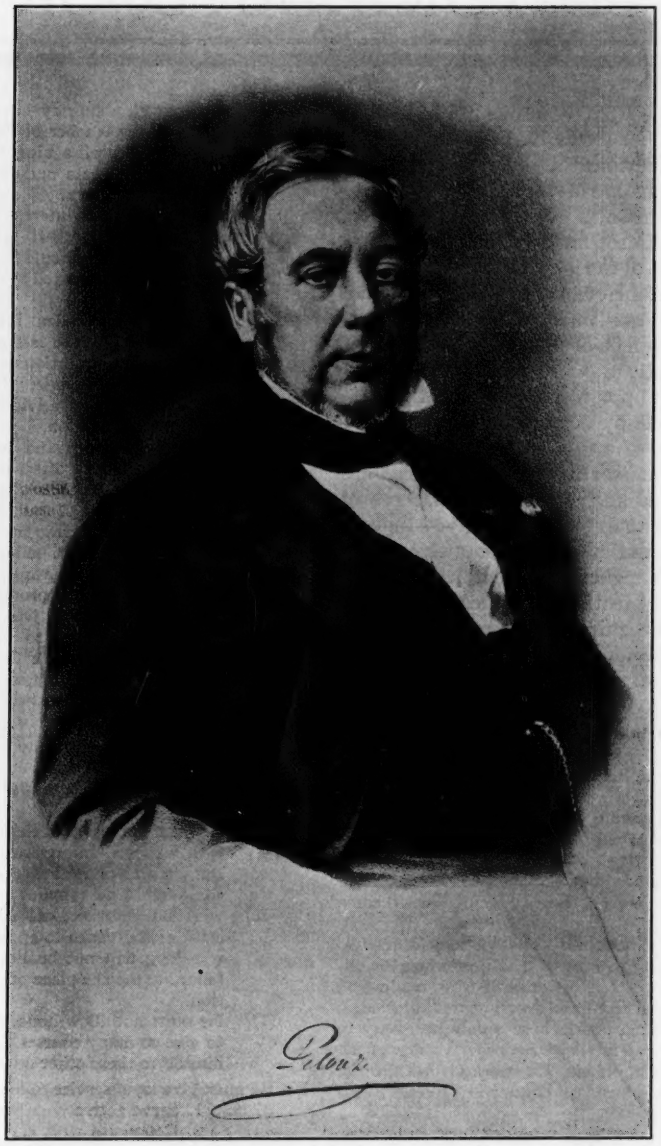

THÉOPHILE-JULES PELOUZE (1807–1867)

Professor at the Collège de France and the École Polytechnic. He made many important contributions to inorganic and to organic chemistry, among which the preparation of ethyl hydrogen phosphate, 1833, and of the first nitrile (propionitrile from barium ethyl sulfate and potassium cyanide), 1834, the isolation of borneol, 1841, and the production of the first artificially prepared fat, glyceryl tributyrate, 1844, are especially notable. He also made important improvements in the process for the manufacture of plate glass, 1856. It was in the laboratory of Pelouze that nitroglycerin was first prepared in 1847 by Sobrero of Turin.

(*Contributed by Tenney L. Davis.*)

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EDITOR'S OUTLOOK

THE IDEAL PROFESSOR OF CHEMISTRY IN THE SMALLER COLLEGE. Borrowing a trick from the répertoire of the newspaper columnist, we are permitting one of our correspondents to do our stint for us this month. As he points out, we have never undertaken to set forth in these columns a summary of the qualities of the ideal chemistry teacher; frankly, we have quailed before the task whenever the notion fleeted through our mind. Our contributor, however, has had the benefit of many years of experience in educational institutions of various sizes, and he has often been called upon to ponder over the questionnaire blanks sent out by accrediting agencies and other organizations.

The duties of the professor in the small college are considerably more varied and extensive than those of his academic brother in the great university. Indeed, our correspondent believes that the doctor of philosophy who has obtained all his higher education in a large institution is often a misfit in the smaller college simply because he does not recognize all his responsibilities. At any rate, here is the ideal small-college chemistry professor in outline.

I. (A) He is well prepared by graduate work, loves his work, has a fine personality, and is conscientious about his teaching duties.

(B) In order to teach well he must keep up to date in his subject matter, which implies:

1. The habit of reading scientific journals and books.
2. Membership in the A. C. S. and subscription to its journals.
3. Some attendance at A. C. S. and section meetings. One always leaves these meetings with some benefit.
4. Work at some research. There is some difference in one's ability to present a subject when the entire knowledge of it is obtained from reading as compared with first-hand experimental knowledge. To find research problems it is only necessary to begin writing an intensive review of a phase of the science, and problems for research within the scope of equipment at hand will present themselves.
5. If possible, consulting work for local industries. The teacher of general chemistry should have a wide knowledge of chemistry. Consulting work widens his knowledge. He will also find the attitude of business men toward technologists illuminating.

(C) He should not forget the objectives of each course, and in curriculum construction the function of each course. He should remember that the progress of chemistry was delayed until men had learned to think scientifically and that, therefore, it is his duty to teach his students to think scientifically. Students not majoring in chemistry should be impressed with the value of research and the usefulness of the chemist.

(D) He must keep up to date professionally as a teacher; that is, he must take note of professional trends. The best way in which to do that is to subscribe to and he JOURNAL OF CHEMICAL EDUCATION. The teaching of chemistry has its own peculiar problems; therefore the teacher of chemistry should be prepared to protect himself against the pseudo-specialist in education who has no understanding of the problems of teaching chemistry.

(E) He should take an interest in the undergraduate science or chemistry club. If these clubs have educational value the faculty should support them.

(F) He should be interested in the career and progress of his students:

1. The gifted student is advised to go on with graduate study; the less gifted student is confronted with his limitations and his abilities and receives appropriate advice; the student with little chemical ability is advised to enter some other field of specialization.
2. The necessity and advantages of taking mathematics must often be explained to the student majoring in chemistry.
3. He explains the advantages and benefits derived from membership in scientific societies.
4. He gives advice on how to obtain employment and helps the graduating student get a job.
5. He is fair and prompt in writing recommendations to prospective employers. He recommends the right man to the inquiring employer. He promptly gives a fair estimate of the student's ability to the inquiring medical school.
6. He listens to the problems of his alumni and helps them with advice.

(If the smaller college offers any advantages because of its size it is because of these personal contacts. The men teaching in them should be of such caliber that contact with them is worth while.)

(G) He must see to it that the library is adequately supplied with journals, and reference and other chemical books. Further, he may be required to see that adequate equipment and supplies are at hand.

(H) He should not neglect other branches of science and learning, but learn to appreciate them in order that his efficiency will not be limited by his narrowness and failure to see the place of chemistry in modern civilization.

(I) He must not allow himself to be tempted or persuaded to give so many courses that he has no time to devote himself to these other duties.

II. He must give loyal service to his institution in a general way:

1. Serve actively on faculty committees.
2. Coöperate with the other departments in every way.
3. Give such special lectures as required.
4. On occasion act as chaperon. Strictly speaking, his wife does that for him.

III. He serves the community and society:

1. Directly, by giving advice to the municipal administration.
2. By giving lectures to groups that desire them.
3. By advancing science by means of publications, the preparation or translation of abstracts, etc.
4. By leadership in church or civic organizations.

"The man who can do all these things all the time and still find time for his family and social obligations is indeed the ideal professor," concludes our correspondent. "Amen," say we.

The MOTORSHIP *CATALYST*— *A* SEAGOING LABORATORY*

THOMAS G. THOMPSON

Oceanographic Laboratories, University of Washington, Seattle, Washington

THE campus of the University of Washington comprises approximately five hundred acres and borders on Lake Washington and Lake Union. These freshwater lakes are connected with Puget Sound by means of one of the largest lock systems in the world. The waters of Puget Sound lead to the thousands of miles of estuaries and inside passages of British Columbia and Alaska and to the vast reaches of the Pacific Ocean. With the sea practically at the gates of the campus, it is but natural that the University of Washington should be attracted by the numerous scientific problems presented in the contemplation of the sea and the life contained therein.

The Oceanographic Laboratories were created to foster the study of the sea. These laboratories are an interdepartmental organization, the staff of which is composed of members from the departments of physics, chemistry, bacteriology, botany, and zoölogy. Besides the main laboratory situated on the shore of Lake Union, there are the field laboratories located near the town of Friday Harbor in the San Juan Archipelago, where much of the work of the summer months is performed and where courses are given in the various sciences. The field laboratories comprise about ten buildings of hollow-tile construction, fully equipped for various types of scientific work and situated on a 480-acre tract with about two miles of shore line. Another integral part of the organization is the floating laboratory or research vessel, the motorship *Catalyst*. It is the object of this paper to give a description of the latter and a brief résumé of the type of work performed aboard.

The research chemist, accustomed to thinking of scientific work in terms of a well-equipped laboratory, can readily appreciate the difficulties of carrying out chemical research on the high seas, especially if he has experienced an ocean voyage. Aboard ship, the laboratory, with its special design of working space and equipment, does not have the stability of the laboratory built upon terra firma, and numerous problems of operation unknown in the land laboratory arise. Even the lingo is modified and the chemist, who is experiencing for the first time a more or less rhythmic motion of the laboratory, may look aghast when his sea-going colleague informs him that the Erlenmeyer flask to the port of his starboard buret appears as if it were going to drag its anchor.

Many of the difficulties presented by an unstable laboratory have been met in the construction of boats for the express purpose of studying the sea from the physical, chemical, biological, and geophysical standpoint and by the construction of special equipment. The former *Carnegie* of the Carnegie Institution of Terrestrial Magnetism, the *Atlantis* of the Woods Hole Oceanographic Institution, the *Scripps* of the Scripps Institution of Oceanography, and the *Catalyst* of the University of Washington, are representatives of the various types of boats used for scientific purposes other than for hydrographic surveying and for fisheries investigations.

The *Catalyst*, besides having much of the regular oceanographic equipment, is unique in the compactness of its laboratory equipment. The boat was designed by the marine architects, Rowland and Strickland of Seattle, and its construction was made possible by funds provided by the Rockefeller Foundation. Many of the features of the laboratory were the suggestions of Dr. Rex J. Robinson and of former students of the author, especially Dr. Bertram D. Thomas, who were obliged to carry on investigations on boats which were anything but ideal for chemical work. Visits to many of the marine laboratories of foreign countries and inspection of their floating equipment by the author yielded information and suggestions of considerable value in the design of the vessel. The *Catalyst* was placed in operation in June, 1932, and since that time has cruised some 25,000 miles and has experienced many and varied conditions of operation.

The principal dimensions of the *Catalyst* are: length over all, 75 feet; length at water line, 72 feet; beam, 18 feet; and draft, 9 feet. Figure 1 shows the general deck plans of the vessel. The hull is of heavy construction and is designed to eliminate motor vibration. The frame is of oak, the double planking of Alaska yellow cedar, and the finish of teak. The keel is of Douglas fir with a two-inch heel of Australian ironbark and, for two feet at the water-line, the boat is sheathed with ironbark. The gross tonnage is 92 tons. The boat is driven by a Washington-Estep full Diesel engine of 120 H.P. at 450 P.P.M., giving a speed of about 8.2 knots and a cruising range of 3500 miles. The engine may be controlled from the pilot house, making it possible for one man to operate the boat if necessary. The engine room is situated almost amidships in order to reduce vibration to a minimum. Located within it are much of the auxiliary apparatus, such as a battery

* Presented before the Division of Chemical Education at the ninetieth meeting of the American Chemical Society, San Francisco, August 21, 1935.

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of 56 marine storage cells for supplying 110-volt direct current, a 3.5-kilowatt generator driven by the main engine when the boat is under way, a 5-kilowatt generator operated by a small, full Diesel Lister engine, two large fuel tanks for Diesel oil, each having a capacity of 1250 gallons, a small tank for lubricating oil, two tanks for compressed air, a hot-water system fired by an oil burner for heating the boat, electrically driven salt-water, fresh-water, and bilge pumps, two electrically driven winches containing the cables for sampling and dredging, and two cylinders of carbon dioxide for use in case of fire.

Sixteen persons may be accommodated aboard. There are six bunks in the forecastle, the captain's bunk in the after part of the pilot house, and four staterooms aft, two for two persons each, one for one, and

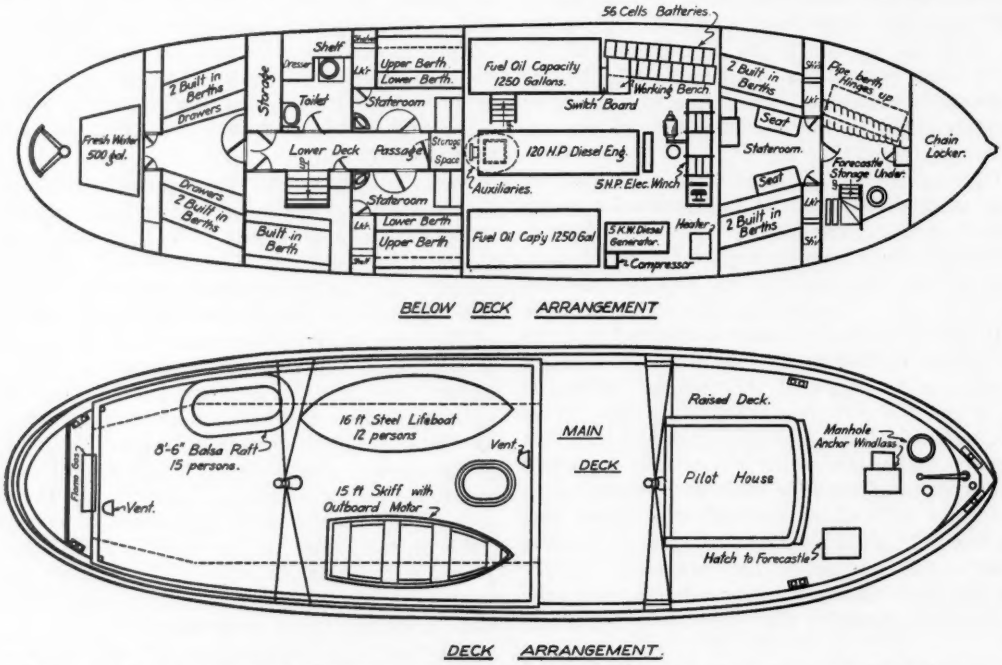

FIGURE 1.—PLAN OF THE *Catalyst* SHOWING THE GENERAL ARRANGEMENT BELOW DECKS AND THE BOAT DECK

one for four persons. Ample locker space, many book-racks, several desks, and hot and cold water are provided, together with many details that add materially to individual comforts. Special attention was given to means for sufficient and proper ventilation to all parts of the vessel by means of forced drafts.

The galley is located in the after end of the deck house and on the main deck. It is equipped with a Flamo gas range with a thermostatically controlled oven, an automatic water heater, and a gas-operated refrigerator. Eight persons may be served at a sitting in the galley, the furnishings of which are all in teak.

Besides the usual equipment found in the average pilot house, there is a fathometer capable of taking 18 soundings a minute down to a depth of 400 fathoms while the boat is under way, the soundings being indicated on a revolving dial by means of a flash of a neon light. The fathometer operates as follows. On the bottom of the hull of the vessel is a device, electrically operated, capable of emitting a sound generated by the blow of a hammer. The sound travels through sea water at a velocity of about 4700 feet per second (the velocity of sound is a function of the temperature and the concentration of the dissolved salts in the water, thus for very accurate soundings in the deeper waters a correction for variations in these factors should be made). The sound of the hammer blow is echoed back from the sea bottom to the surface, the echo picked up by a delicate telephone-like receiver, and the impulse amplified so that an electric contact is made with a small neon tube attached to a revolving disc. The outgoing sound registers a thin line of red light at zero on the dial and a fraction of a second later the echo produces another red flash which, on the scale of the dial, indicates the depth of the water.

The *Catalyst* is steered with a photo-electric pilot which is capable of keeping the ship on its course more accurately than the best helmsmen. The photo-electric pilot consists of: (1) a directive element, which is a binnacle carrying a light train and a photo-electric cell; (2) an amplifier and relay control box; (3) a reversing-type series motor for moving the wheel controlling the rudder; (4) a steering clutch, which ties the binnacle and the ship's rudder together; (5) a course-changing differential capable of regulating the

course of the ship to a quarter of a degree; and (6) a dodger or displacement switch.

The directive element is a binnacle with a magnetic compass, having a special card with half its rim cut away. On top of the compass bowl a light, lens, and mirror are mounted in such a manner that light passes through the portions of the special card where the rim has been cut away, and falls on the photo-electric cell mounted on the underside of the bowl. The binnacle may move so that the rim of the card will not permit the passage of any light. A photo-electric cell has the characteristic of passing current in proportion to the light falling upon it. This variation in current due to the variation in light intensity falling upon the cell gives the means for controlling the operation of the motor connected with the steering apparatus. When the ship is exactly on its course, a given intensity of light falls on the photo-electric cell and the motor will be idle. If the ship swings in such a direction as to uncover more light, a relay closes and starts the motor which turns the rudder. As the boat swings, the binnacle moves in the direction to cover the light to the proper intensity, bringing the ship on its course, the motor becoming idle. However, as the ship comes back to its course it may swing too far in the other direction, decreasing the light intensity. A relay closes and starts the motor turning in the opposite direction, the binnacle moving to permit greater light intensity. The course of the ship is supposedly a straight line but in reality an undulating line is produced along the course traveled. The magnitude of departure from a straight line, however, is far less with the photo-electric pilot than with a human being at the wheel of the ship.

In following a course, should an obstruction such as a floating log appear, the dodger switch is used. When the switch is pressed to the left, the ship swings rapidly to port, or, if the obstruction is to be passed on the port, the switch is pressed to the right and the ship swings to starboard. Upon release of the switch, the ship automatically comes back to its original course.

The outstanding feature of the *Catalyst* is the laboratory which occupies the forward part of the main deck house. It is 19 feet long and 10 feet 6 inches wide. Figure 2 is a general floor plan of the laboratory. This rather small space has been utilized to such an advantage as to provide desk space for seven persons, the laboratory benches running fore and aft on each side. The benches are marked off into seven convenient sections by sets of drawers placed under the benches. Each desk section is equipped with a Duriron drain, three electric outlets, one each for 110 volts A.C. and D.C. current and one for a variable voltage, and an outlet for Flamo gas. The direct current is supplied from the ship's batteries and the alternating current from a 0.5-kilowatt alternator operated from the direct-current line. Flamo gas is carried in tanks on the after part of the main deck house. Two outlets supply compressed air at 8 pounds pressure and are conveniently located, one at each end of the laboratory. All the shelving for numerous reagent bottles is especially constructed so that the bottles will remain in place despite the pitch and roll of the ship. Each of the drawers and the several cabinets is partitioned to prevent movement of glassware and other materials. In the after part of the laboratory is a lead-lined sink, with a Duriron drain, and outlets for salt and fresh water. A shelf near the sink contains the bottle supplying distilled water. Immediately above the sink is a fume-hood with seagoing hot plates electrically operated. Compartments on the hot plates enable evaporations to be made without any shifting of the apparatus due to the movement of the boat. A Duriron blower installed atop the boat deck supplies the draft for the hood. Further ventilation of the laboratory is provided by reversible fans.

The vibration from the engine, while the boat is under way, is so slight that one may readily make quantitative counts with a microscope. Figure 3 is a view of the interior of the laboratory, looking forward, and shows Dr. John E. Guberlet, professor of zoölogy, examining some zoöplankton under the microscope. The racks for the reversing thermometers are seen in the background, and to the left of these are racks containing two of the twelve water-sampling bottles. Figure 4 shows the laboratory, looking aft, with Dr. Rex J. Robinson of chemistry making a titration.

The radiators for heating the laboratory are built-in vertical ducts back of the benches. An excellent indirect lighting system has been provided. The deck

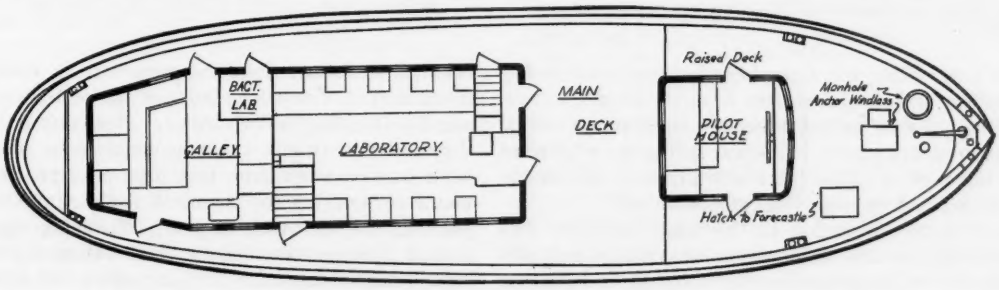

FIGURE 2.—PLAN OF THE MAIN DECK OF THE *Catalyst* SHOWING THE LOCATION OF THE PILOT HOUSE, LABORATORY, AND GALLEY

of the laboratory is of acid-resisting material, and Duriron floor drains lead directly overboard. The entrance to the laboratory is from the forward end of the deck house and an escape hatch, for emergencies, leads to the boat deck. The door of the laboratory opens immediately onto the main deck. This work deck, which is clear the width of the vessel, is shown in Figures 5 and 6. Here water samples are secured, various pieces of apparatus for making physical and chemical measurements are lowered into the sea, and different types of net hauls, dredging of the sea floor, and bottom-sampling are conducted. On each side of the deck house, on the outer deck, are a number of outlets for running sea water and for compressed air. Long, narrow portable tanks are lashed under the outlets to the deck and in them are placed biological specimens which are to be taken alive to the shore laboratories. The water may be aërated by means of compressed air.

Early in the operation of the boat, difficulty was encountered in the preparation of various cultures because of the occasional use of formaldehyde in the main laboratory. To avoid this difficulty, the deck lavatory was altered so that it could be readily converted into a small bacteriological laboratory by providing movable benches that could be lashed to the sides when not in use and installing a gas outlet. Hot and cold water had already been provided. Figure 7 shows a bacteriologist in his improvised laboratory.

At the forward end of the engine room are two winches, driven by a five-horsepower motor, which carry the cables for sampling operations and for dredging. These winches are controlled by levers situated on the main deck. On the drum of one winch is 4500 meters of $^{5}/_{16}$-inch stainless steel cable which permits sampling to a depth of three miles. This cable is used for the water-sampling apparatus for chemical and bacteriological purposes, for vertical and horizontal net hauls for plankton, for bottom sampling, and for sounding in deep water. This cable has proved very resistant to salt water during the four years it has been in operation and has been a very important factor in securing for chemical study samples free of particles of iron rust, copper, oil, and grease. The second drum contains 600 meters of half-inch galvanized cable which is used for dredging plant and animal life existing on the bottom of the passages, estuaries, and the continental shelf.

The cables run from the drums below deck over

FIGURE 3.—VIEW OF THE LABORATORY ON THE *Catalyst* LOOKING FORWARD

FIGURE 4.—VIEW OF THE LABORATORY ON THE *Catalyst* LOOKING AFT

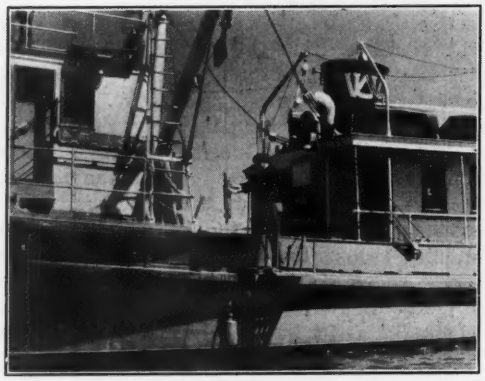

FIGURE 5.—VIEW OF THE PORT SIDE OF THE *Catalyst* SHOWING THE PLACING OF WATER-SAMPLING BOTTLE ON CABLE

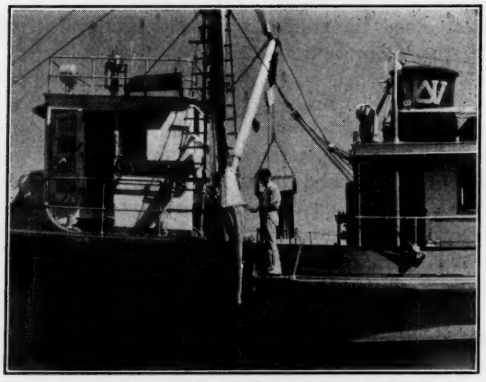

FIGURE 6.—VIEW OF THE PORT SIDE OF THE *Catalyst* SHOWING THE HENSEN CLOSING NET USED FOR COLLECTING PLANKTON

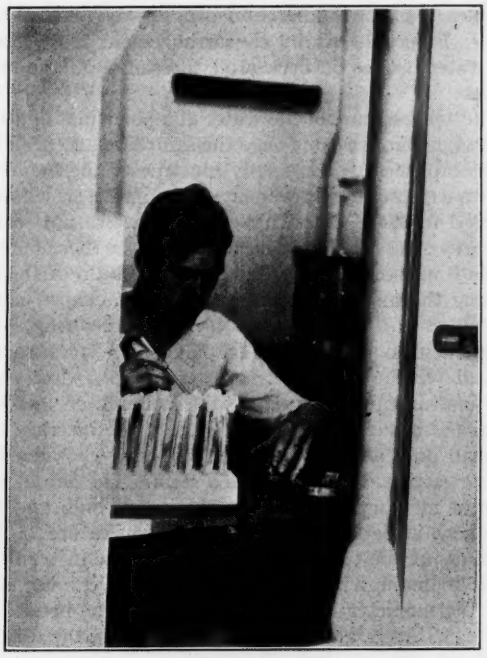

FIGURE 7.—MAKING BACTERIOLOGICAL CULTURES IN THE LABORATORY ON THE *Catalyst*

shives attached to the foremast and to the booms suspended from it. The latter may be lowered over both sides of the vessel. Both cables pass over meter wheels which record the length of the cable lowered over the ship's side. Projecting from each boom is a compensator with a shive attached to the lower end, over which the cable passes to enter the water. These compensators relieve the stresses and strains of heavy loads during the roll of the vessel. All the shives are of the large cargo size with which there is not the excessive bending of the cable characteristic of smaller shives.

Figure 8 is a bow view of the *Catalyst* showing the arrangement of the booms, compensators, and shives. Figure 5 shows the port side of the vessel amidships and the pulpit or sampling platform which projects from the side of the vessel; the apparatus for securing water samples and for measuring the temperature is being placed on the cable. Figure 6 illustrates the type of net used for securing the very small phyto- and zoöplankton occurring in the sea. For example, this net is lowered to the desired depth, say 1000 meters, and then drawn upward to 500 meters where the net is closed by a metal messenger sent down the cable. It is then brought aboard without contamination from any of the organisms in the upper water layers and yields only plankton found in the layer between 500 and 1000 meters.

The dredge operated from the starboard side of the vessel is shown in Figure 9. The collecting bag of the dredge is made from netting which is attached to an iron frame. The comparatively fragile net is armored

FIGURE 8.—BOW VIEW OF THE *Catalyst* SHOWING ARRANGEMENT OF BOOMS AND COMPENSATORS

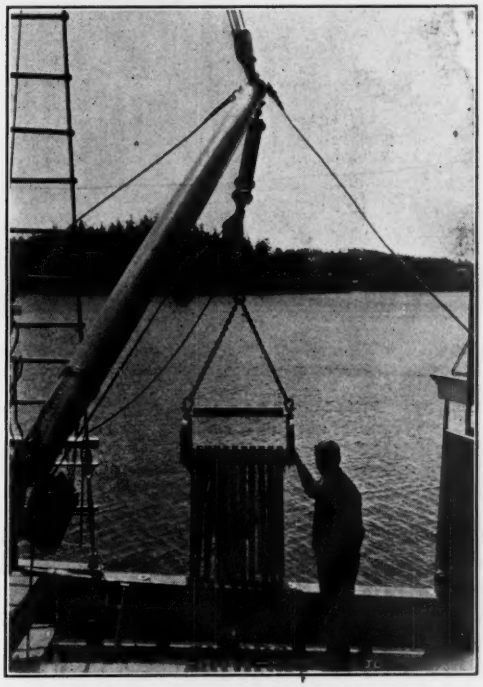

FIGURE 9.—VIEW OF THE STARBOARD SIDE OF THE *Catalyst*
Showing type of dredge used to secure biological specimens from the sea floor. The detail of the shive arrangement and compensator is shown.

with long brass strips to protect it from the rocky floors characteristic of many of the passages of the northeast Pacific.

The *Catalyst* carries the usual life-saving equipment such as a lifeboat, life raft, life preservers, and a skiff. The vessel is equipped with a 500-pound anchor with 120 fathoms of anchor chain, auxiliary anchors, sea anchors, and an electrically operated anchor winch.

The crew consists of the captain, engineer, and cook. Several deck hands, who are students with sea experience, have their duties divided between scientific

work and the ordinary operation of the ship. On extended cruises, everyone aboard is assigned to certain boat duties in addition to the scientific work in which he is particularly engaged.

The chemical work performed aboard ship is often more or less routine in nature except where it supplements the more extensive and elaborate studies conducted in the shore laboratories. Samples of water are collected in a water bottle of the Nansen type (as shown in Figure 10), having a capacity of two and one-half

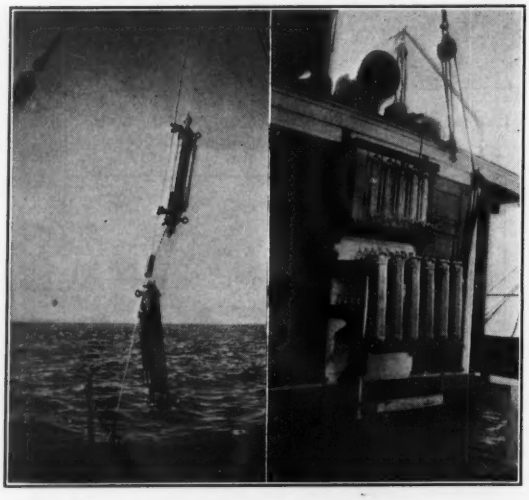

FIGURE 10 (LEFT).—WATER BOTTLES USED IN THE COLLECTION OF SAMPLES OF WATER BELOW THE SURFACE OF THE SEA

Top bottle is in position for sampling. The lower bottle shows position after the sample has been secured.

FIGURE 11 (RIGHT).—ARRANGEMENT FOR RACKING THE WATER BOTTLES ON DECK AFTER THE SAMPLES HAVE BEEN TAKEN

liters. Attached to the side of the bottle are two open, armored tubes of metal in which thermometers may be placed. The bottles are of bronze and are plated heavily, either with nickel or silver. This sampling apparatus is clamped to the cable and held in position by a movable pin. The hinged ends of the bottle are open as shown in the upper bottle in the illustration. The bottle is lowered in this position to the desired depth. A messenger is then placed on the cable and slides down the wire until it strikes the bottle. These messengers sink at the rate of about 200 meters a minute. Because of the impact, the springs that hold the top and bottom of the covers in place are released and the covers snap down, enclosing the sample of water. At the same time the movable pin is released, the top of the bottle falls from the line assuming the position illustrated by the lower bottle in the cut. This latter movement is essential in recording the temperature, as will be described. As it is desirable to take several samples simultaneously at different depths, a number of the bottles may be placed on the cable for one series of sampling. On the *Catalyst* a series of 15 samples at as many different depths may be taken at one time. Figure 11 shows the arrangement for racking the water bottles on deck after the samples have been taken.

The temperature of the water at a particular depth is ascertained at the same time the sample is taken. This is accomplished by a specially constructed thermometer known as a protected reversing thermometer which may be read to 0.005°C. These thermometers are sealed in heavy glass tubes in order to protect the thermometer bulbs from pressure effects. The large bulb of the reversing thermometer is immersed in a mercury jacket contained in the heavy glass tube, thus insuring rapid temperature equilibrium. A capillary tube is contracted just above the large thermometer bulb, so that when the instrument is inverted, the column of mercury breaks at a particular point. Part of the mercury fills a small bulb at the top of the reversing thermometer and a portion of the graduated stem. The actual volume of mercury flowing into this small bulb and the capillary is dependent upon the temperature of the mercury at the time of the reversal of the instrument. Thus to make a temperature reading, the reversal of the thermometer is essential in order to break the mercury thread, and hence the necessity for the turning of the bottle at time of sampling. By reading the graduated scale on the reversed thermometer, the temperature may be ascertained. Certain corrections, which are too detailed to be discussed here, are necessary before the actual temperature of the water *in situ* can be ascertained.

The approximate depth to which the bottles are lowered may be observed from the reading of the meter wheel. However, during the process of sampling, the boat may be subjected to a drift and thus the wire cable, instead of being exactly perpendicular to the ship, may be at an angle. To learn the exact depth at which a sample is obtained, or at which temperature readings are made, an unprotected thermometer is used and is set in the thermometer frame beside the protected thermometer. Because of the protection afforded by the heavy glass tube in which the protected reversing thermometer is incased, pressure has no effect upon the mercury bulb. In the case of the unprotected reversing thermometer, the mercury bulb of the main thermometer is not thus protected from the pressure. This pressure, which is a function of the depth and the density of the water, causes mercury to be forced into the upper portion of the thermometer in addition to that resulting from thermal effects; thus, when this thermometer is reversed, the reading on the temperature scale will be considerably higher than that of the protected thermometer. From the data secured by the protected and unprotected thermometers and analyses of the waters it is possible to calculate the depth with considerable accuracy, when the pressure constant of the unprotected thermometer is known.

It has been found that the major constituents of sea water, regardless of the depth or the section of the world from which a sample is obtained, exist in definite

ratios to one another. Thus the measure of a single constituent may be regarded as the measure of the relative concentration of the water. The halide ions are the most abundant and most easily and accurately determined. The determination of these halides is accomplished by titration with silver nitrate using potassium chromate as the indicator. The halides are calculated as chlorides and the resulting value is known as the chlorinity. A definite relationship thus exists between the chlorinity, total concentration of dissolved salts, the major individual constituents, and the physical properties of the water.

The physical properties of sea water are a function of the temperature, the pressure, and the concentration of the dissolved salt. Very accurate determinations of the specific gravity of sea water at 0°C. have been made for various concentrations of chlorinity. Knowing the density at 0°C., the density of a water at any other temperature for a given chlorinity may then be calculated.

The compressibility of water is so exceedingly small that for most practical purposes in scientific considerations corrections for compressibility are invariably disregarded. This is not so in dealing with the sea. If water were absolutely non-compressible, sea-level would be ninety feet higher than it actually is. Thus in ascertaining the density *in situ* of water at great depths, this compressibility of water must be taken into consideration.

By the application of the Bjerknes circulation theorem, it is possible to calculate the resultant flow of ocean currents in relation to the bottom water from the data obtained by the titration for the halides and the temperature observations.

Many persons have an idea that sea water is nothing more or less than a solution of common salt or sodium chloride. This is not the case, as shown by the composition of sea water given in the accompanying table. The average chemist generally expresses concentration as normality or molarity per liter of solution or as gram-molecular weight per kilogram of solvent. In oceanographical chemistry, because of variations in density, the concentration is expressed as grams or milligrams per kilogram of sea water (solution) or as milligram atoms per kilogram of sea water.

In correlation with biological observations, the distribution of certain nutrient salts, which serve as fertilizers for marine plants in much the same manner as for land plants, is of marked interest to the chemist. The occurrence, distribution, and rôle of a number of elements occurring in the sea, which have received no attention or only scant consideration, offer fascinating problems for study. The biochemist is interested in the absorption and utilization of the many elements by the plants and animals and in the chemical reactions and energy changes of metabolism of the greatly varied marine life. The nature and the mechanisms of the formation of marine deposits attract the geochemist. The determination of a number of physical-chemical constants, and the regularity of their variation with the changes in concentration, temperature, and pressure, is of great importance for the interpretation of the physiology of marine organisms, and some are of marked use in the rapidly growing science of meteorology. The study of the complex solution, sea water, may be instrumental in arriving at a satisfactory theory of solutions. From the chemical engineering viewpoint there is interest in the possible recovery and utilization of a great number of chemical products obtainable in the sea. One of the oldest industries is the preparation of sodium chloride from sea water, and among the most recent is the recovery of bromine and the preparation of a number of magnesium compounds.

THE APPROXIMATE COMPOSITION OF SEA WATER WITH A CHLORINITY OF 19.00%

	Milligram Atoms per Kilo. of Sea Water
Chlorine	535.0
Sodium	454.0
Sulfur (sulfate)	27.63
Magnesium	52.30
Calcium	10.19
Potassium	9.6
Carbon (bicarbonate and carbonate)	2.45
Bromine	0.81
Boron	0.43
Strontium	0.15
Aluminum	0.07
Fluorine	0.068
Silicon (varies)	0.05
Lithium	0.015
Nitrogen (nitrate, varies)	0.014
	($\times 10^3$)
Phosphorus	300.0
Copper	200.0
Barium	150.0
Iron (varies)	38.0
Iodine (varies)	35.0
Silver	20.0
Manganese	10.0
Nitrogen (nitrite)	0 to 10
Arsenic	4.0
Zinc	3.0
Hydrogen Ion	1.0
Selenium	0.5
Gold	0.025

In this paper no attempt has been made to describe the use of the *Catalyst* in promoting the solution of many biological problems and the study of the ever-interesting distribution of the varied animal and plant life of the sea. The vessel has been described and an attempt has been made to summarize briefly the rôle of the chemist in the study of the medium that covers approximately seventy per cent. of the surface of the world.

OUTLINE OF ESSENTIALS FOR HIGH-SCHOOL CHEMISTRY

For the benefit of those who may desire additional, or more convenient, copies of the recent report of the Committee on Correlation of High-school with College Chemistry, the Division of Chemical Education has prepared a limited reprint edition to be sold at cost (10 cents each, with special prices on quantities). Orders, with remittance, should be sent to Journal of Chemical Education, % the Mack Printing Co., 20th and Northampton Streets, Easton, Pa.

The MAGNETO-OPTIC METHOD *of* CHEMICAL ANALYSIS

I. HISTORY AND PRESENT STATUS OF THE METHOD

STANCIL S. COOPER WITH T. R. BALL

Washington University, St. Louis, Missouri

INTRODUCTION

THE magneto-optic method of chemical analysis has been the subject of controversy for several years largely because many observers have been unable to reproduce the experimental data published and have been unable to arrive at a satisfactory explanation of the magneto-optic effect on purely theoretical grounds. Those who have been successful in operating the apparatus believe that numerous failures have resulted either from set-ups which were not functioning properly or from the lack of realization on the part of the observers of the many difficulties that confront them. It seems advisable, consequently, to present the method in more detail than has been done hitherto in the hope that the experiences of the authors may prove valuable to those who attempt to apply it.

This series of articles will present the historical development of the method, its present status, and the construction and operation of the apparatus. The method used in overcoming many of the difficulties encountered in the solution of a chemical problem by the use of the apparatus will also be given.

The magneto-optic apparatus is perhaps the most important tool for chemical research developed in the last decade. The extreme sensitivity of the apparatus to the presence of compounds adapts it admirably to the solution of problems involving very low concentrations. It will detect the presence of a substance in a concentration as low as a few parts in 10^{12}.

A careful study of the positions of minima in relation to the compounds producing them has revealed an orderly relationship between equivalent weights and minima positions. Thus the magneto-optic method of chemical analysis has been evolved and has been extended both qualitatively and quantitatively. It agrees with standard methods of quantitative analysis within a few per cent. In repeated qualitative analyses it has shown an accuracy of eighty to ninety per cent. on solutions far too dilute to be analyzed by ordinary methods. It is doubtful if any single method, or combination of methods, is superior to this in these two fields when very low concentrations are involved.

The method presents interesting and important features in addition to its extreme sensitivity and its dependability. The speed with which analyses may be made exceeds that of the majority of methods. Furthermore, the sample is merely subjected to a beam of light passing through it and is not destroyed by the analysis. In addition, substances which are very slightly soluble lend themselves readily to analysis, inasmuch as very small quantities are easily detectable. Intermediates also may be determined, the concentrations of which at any time during the course of a reaction are too low to be detected by other methods. The apparatus will detect the presence of isotopes of a positive element and the order of abundances of these isotopes can be determined. Changes in concentrations during slow reactions and the determination of equilibrium constants are indicated as possible fields for further research. Preliminary work has indicated that the apparatus may be employed for the qualitative and quantitative analysis of substances for their vitamin content. In the field of physiological chemistry there is need of intensive work with the apparatus.

Although inorganic compounds in large numbers have been thoroughly investigated on the apparatus and their minima positions well established, organic compounds have been little studied. Positions of minima have been determined for some aliphatic compounds, but little has been done with the aromatic. Investigations in these two series should be extended.

The operation of the apparatus, however, requires of the observer the attainment of a considerable amount of experience and technic.

HISTORY

Faraday,[1] in 1845, discovered that a transparent, isotropic medium when placed in a powerful magnetic field acquires the ability to rotate the plane of polarization of polarized light when the light traverses the medium in the direction of the magnetic force. This phenomenon, known as the Faraday effect, has been observed in solids,[1] liquids,[2] and gases.[3] The phenomenon differs, however, from natural rotation in that the direction in which the plane is rotated is reversed if the magnetic field is reversed; that is, if the

[1] FARADAY, "Experimental researches in electricity," Richard and Francis, Printers, London, **1885**, Vol. III, p. 1.

[2] (*a*) PERKIN, *J. Chem. Soc.*, **45**, 421 (1884); **53**, 561 (1888); **65**, 402 (1894); **67**, 255 (1895); **69**, 1025 (1896); **81**, 292 (1902); **91**, 806 (1907); (*b*) RODGER AND WATSON, *Trans. Roy. Soc.* (London), [2], **186**, 621 (1895); (*c*) VERDET, *Compt. rend.*, **38**, 613 (1854); **39**, 548 (1854); **43**, 529 (1856); **44**, 1209 (1857); **45**, 33 (1857); **56**, 630 (1863); **57**, 670 (1863).

[3] KUNDT AND ROENTGEN, *Wied. Ann.*, **6**, 332 (1879).

plane is rotated clockwise when the light enters by the north pole and leaves by the south pole, it will be rotated counter-clockwise when the light passes in the reverse direction. The magnitude of rotation depends on the strength of the magnetic field parallel to the direction of the light, on the length of the light-path in the medium, and on the medium itself. Thus if H is the field strength and l is the length of the light-path in the medium, then the angle A, through which the plane is rotated, is expressed by $A = KlH$, where K is known as Verdet's constant. The Verdet constant is characteristic of the medium itself and may be expressed as the angle of rotation in minutes per unit field strength per centimeter of light-path in the medium.

Attempts have been made to detect a time interval between the application of the magnetic field and the appearance of the Faraday effect as well as a time interval between the removal of the magnetic field and the disappearance of the phenomenon.

In passing plane polarized light through a piece of glass rotating in a magnetic field Villari[4] observed that the normal Faraday effect decreased as the speed of rotation of the glass was increased. By interpreting this as meaning that a certain time was necessary to establish the Faraday effect, Villari estimated the lag to be between one-four-hundredth and one-eight-hundredth of a second. Lodge[5] has explained that the results of Villari were caused by centrifugal strains induced in the glass. Bichat and Blondlot[6] found that on discharging a Leyden jar through a spark and then a helix, inside of which was a tube of carbon disulfide, polarized light was rotated with each impulse of the oscillatory discharge. The plane in this instance was rotated clockwise and counter-clockwise at the rate of about seventy thousand rotations per second. Half of a slit was illuminated by light coming directly from the spark and the other half by light from the same spark but coming through the carbon disulfide. The illuminated slit was examined in a revolving mirror and was found to be spread out into a serrated band, but no discontinuity was observed in the two portions of the slit. This showed that if a time interval existed it must have been less than 10^{-5} seconds for carbon disulfide. Abraham and Lemoine,[7] using the method designed by them to measure the time required for the development of the electro-optic effect, found that if there was a difference in time between the creation of the magnetic field and the subsequent rotation of the light, this difference must have been less than 10^{-8} seconds for carbon disulfide. In this method damped oscillations from a condenser were passed across a spark-gap, the source of light, through a resistance and thence around a solenoid which contained carbon disulfide.

For many years the existence of a time-lag in the appearance of the Faraday effect was doubted, and not until 1927 was there any evidence that such a lag existed. Beams and Allison,[8] adopting a modification of the method of Abraham and Lemoine,[7] obtained results which indicated that there really exist differences of time from 10^{-9} to 10^{-8} seconds between the application of the magnetic field and the subsequent rotation of the light when certain liquids are used with reference to carbon disulfide. In this method, damped oscillations from a condenser were passed across a spark-gap, which served as the source of light and also as interrupter for the current, and thence through two solenoids, connected in parallel and so arranged that the distance between them could be varied. The polarities of the two solenoids were opposite. One of the solenoids contained carbon disulfide and the other the liquid under investigation. Light from the spark was polarized, passed successively through the two solenoids, and analyzed. The polarizer and analyzer were arranged in a crossed position. When carbon disulfide was placed in both solenoids, light emerged from the analyzer. When, however, the distance between the solenoids was varied, a certain point was reached at which light was extinguished in the analyzer. With the solenoids oriented in this position, one of several liquids was substituted for carbon disulfide in one of them. Light was then observed through the analyzer. By moving the two solenoids farther apart or closer together, a certain point was reached at which the light emerging from the analyzer became a distinct minimum. The difference between these two distances divided by the velocity of light in air represented the time-lag, in seconds, of the Faraday effect in the liquid used referred to carbon disulfide. This differential time-lag was found to vary with the substance employed. When the same substance was used in reference to carbon disulfide, the differential time-lags were found to be some inverse function[9] of the wave-length of the light. The lags were destroyed when X-rays[10] were passed through the liquid under investigation and returned when the X-rays were shielded from the liquid. The lags were unaffected by temperature changes.[9] It was found on further investigation[9] that minima of light intensity could be produced if the two solenoids were separated by a constant distance and the path length of the electric impulse leading to the two cells varied. The difference of the path lengths divided by the velocity of electricity through metallic conductors gave time-lags very nearly identical with those obtained when the light-path alone was varied. For convenience in operation, therefore, the wire-path alone (or a combination of wire-path and light-path) was varied. When the light-path is constant, the wire-path lengths leading to the two solenoids which contain carbon disulfide are those which must be established to produce

[4] VILLARI, *Pogg. Ann.*, **149**, 324 (1873).
[5] LODGE, *Phil. Mag.*, [5], **27**, 339 (1889).
[6] BICHAT AND BLONDLOT, *Compt. rend.*, **94**, 1590 (1882).
[7] ABRAHAM AND LEMOINE, *ibid.*, **129**, 206 (1899); **130**, 499 (1900).
[8] BEAMS AND ALLISON, *Phys. Rev.*, **29**, 161 (1927).
[9] ALLISON, *ibid.*, **30**, 66 (1927).
[10] ALLISON, *ibid.*, (*a*) **31**, 158 (1928); (*b*) **31**, 306 (1928).

electrical and optical balance in the system. This determined wire-path length leading to the carbon disulfide cell (the one nearest the spark) is fixed and the corresponding length to the other cell (the cell carrying the liquid under investigation) is that obtained when the movable trolley is set at 15.00. An increase or decrease in wire-path leading to the second cell is thus marked on the reference scale (1 unit = 15 cm.). Positions along the reference scale necessary to produce minimum light transmissions for certain substances, referred to carbon disulfide, are recorded as minima for those substances.

Minima have been observed for solutions of both inorganic[11] and organic[12] compounds. These minima, for water solutions of inorganic compounds, were found to disappear only after the concentration of the inorganic compound became less than several parts in 10^{12} parts of water.[11a,b] Foreign substances[13] produce no change in the character or positions of the minima. In both inorganic[11a,b] and organic[12d,e] series of compounds positions of the minima have been found to vary directly with the equivalent weight of the positive constituent of the molecule, and inversely with the equivalent weight of the negative constituent. For isotopes[14] of a positive element, minima vary inversely with the equivalent weight of the isotope.

On the basis of the several observations mentioned above, the magneto-optic method of chemical analysis was announced by Allison and Murphy.[11a,b] Because of the extreme sensitivity of the method it has been used in many phases of research, the majority of which involve the detection of minute quantities of substances. The method has been developed both qualitatively and quantitatively.

The discoveries of the last two remaining chemical elements, 87[15] and 85,[16] have been announced from Allison's laboratory. The existence of element 87 was confirmed by McGhee and Lawrenz,[17] by the same method, and by Papish and Wainer,[18] who used X-ray spectral data.

Very fruitful results have been obtained in the detection of isotopes by this method. The detection of hydrogen of mass two was announced by Allison and his co-workers,[19] and later by Urey[20] using the spectroscopic method. Latimer and Young,[21] employing heavy water as a solvent in the magneto-optic method, have detected a hydrogen of mass three. $_1H^3$ has been postulated and experimental evidence has been given by other methods for its existence.[22] The isotopes of many elements[23] have been more or less thoroughly investigated by this method.

In the field of radioactivity the method has led to the detection of the end product of radioactive potassium,[23c,h] namely $_{20}Ca^{41}$ which comes from $_{19}K^{41}$ by the loss of a beta particle, has led to a new radioactive disintegration scheme,[24] and has aided in the interpretation of problems of geologic time.[25]

The application of the method to problems in chemistry gives promise of opening up the most fruitful field so far entered. The number and types of problems to which the method may be applied are almost unlimited. To this end data for minimum positions have been determined for both inorganic[26] and aliphatic organic[12d,e] compounds. Practically every paper published represents the qualitative application of the method. It has been developed quantitatively for calcium,[27] uranium,[28] and copper.[29] The method has been used by Allison, Bishop, and Sommer[16b] to determine the deportment of bromine, iodine, and element 87 toward certain reagents. Hughes and Hopkins[30] have used it to trace the concentration in rare earths, and Ball and Crane[31] to detect intermediate states in the reduction of chromium from chromate to chromic ion. Yoe and Wingard[12c] have employed it in detecting the formation of formaldehyde from irradiated carbon dioxide and water, and Sommer, Bishop, and Otto[12f] in measuring the rate of formation of formaldehyde in the presence of chlorophyll. Jones and Goslin[32]

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[11] (*a*) ALLISON AND MURPHY, E. J., *Phys. Rev.*, **35**, 124 (1930); (*b*) *J. Am. Chem. Soc.*, **52**, 3796 (1930).

[12] (*a*) Ref. 8, p. 164; (*b*) Ref. 9, p. 69; (*c*) YOE AND WINGARD, *J. Chem. Phys.*, **1**, 886 (1933); (*d*) MCGHEE AND LAWRENZ, *J. Am. Chem. Soc.*, **55**, 2614 (1933); (*e*) MCGHEE AND LAWRENZ, *ibid.*, **55**, 4333 (1933); (*f*) SOMMER, BISHOP, AND OTTO, *Plant Physiol.*, **8**, 564 (1933); (*g*) WISSINK AND WOODROW, *Phys. Rev.*, **45**, 126 (1934); (*h*) WISSINK, *Physics*, **5**, 31 (1934).

[13] (*a*) ALLISON, *Phys. Rev.*, **31**, 313 (1928); (*b*) Ref. 11*a*.

[14] (*a*) Ref. 11*a*; (*b*) ALLISON, *Ind. Eng. Chem., Anal. Ed.*, **4**, 11 (1932); (*c*) ALLISON AND MURPHY, E. J., *Phys. Rev.*, **36**, 1097 (1930).

[15] (*a*) ALLISON AND MURPHY, E. J., *Phys. Rev.*, **35**, 285 (1930); (*b*) ALLISON, BISHOP, AND SOMMER, *J. Am. Chem. Soc.*, **54**, 613 (1932).

[16] (*a*) ALLISON, MURPHY, E. J., BISHOP, AND SOMMER, *Phys. Rev.*, **37**, 1178 (1931); (*b*) ALLISON, BISHOP, AND SOMMER, *J. Am. Chem. Soc.*, **54**, 616 (1932).

[17] MCGHEE AND LAWRENZ, *J. Am. Chem. Soc.*, **54**, 405 (1932).

[18] PAPISH AND WAINER, *ibid.*, **53**, 3818 (1931).

[19] (*a*) Ref. 14*b*, p. 11; (*b*) ALLISON, *Am. Inst. Mining Met. Eng.*, Preprint, New York Meeting, Feb., 1932; (*c*) ALLISON, J. CHEM. EDUC., **10**, 71 (1933); Ref. 16*a*.

[20] UREY, BRICKWEDDE, AND MURPHY, G. M., *Phys. Rev.*, **39**, 164 (1932).

[21] LATIMER AND YOUNG, *ibid.*, **44**, 690 (1933).

[22] OPIHANT, HARTECK, AND RUTHERFORD, *Nature*, **133**, 413 (1934); LOZIER, SMITH, AND BLEAKNEY, *Phys. Rev.*, **45**, 655 (1934); HARNWELL, SMYTH, VAN VOORHIS, AND KUPER, *ibid.*, **45**, 655 (1934); TUVE, HAFSTAD, AND DAHL, *ibid.*, **45**, 840 (1934).

[23] (*a*) Ref. 14*c*; (*b*) BISHOP, *Phys. Rev.*, **40**, 16 (1932); (*c*) ALLISON AND GOSLIN, *ibid.*, **40**, 1015 (1932); (*d*) BISHOP, LAWRENZ, AND DOLLINS, *ibid.*, **43**, 43 (1933); (*e*) ALLISON AND BISHOP, *ibid.*, **43**, 47 (1933); (*f*) BISHOP AND DOLLINS, *ibid.*, **43**, 48 (1933); (*g*) GOSLIN AND ALLISON, *ibid.*, **43**, 49 (1933); (*h*) LATIMER AND YOUNG, *ibid.*, **44**, 61 (1933); (*i*) BISHOP AND ALLISON, *ibid.*, **44**, 419 (1933); (*j*) YOE, *ibid.*, **44**, 420 (1933); (*k*) BALL AND COOPER, *J. Am. Chem. Soc.*, **55**, 3207 (1933); (*l*) OTTO AND BISHOP, *ibid.*, **55**, 4371 (1933); (*m*) DOLLINS AND BISHOP, *ibid.*, **55**, 4372 (1933); (*n*) SNODDY, *Phys. Rev.*, **44**, 691 (1933).

[24] BISHOP, *Phys. Rev.*, **43**, 38 (1933).

[25] PIGGOT, *ibid.*, **43**, 51 (1933).

[26] Ref. 11*b*, p. 3798 and many others.

[27] (*a*) BISHOP AND DOLLINS, *J. Am. Chem. Soc.*, **54**, 4585 (1932); (*b*) BISHOP, DOLLINS, AND OTTO, *ibid.*, **55**, 4365 (1933).

[28] JONES AND GOSLIN, *Am. J. Physiol.*, **105**, 693 (1933).

[29] BISHOP, OTTO, AND BLAISDEN, *J. Am. Chem. Soc.*, **56**, 408 (1934).

[30] HUGHES AND HOPKINS, *ibid.*, **55**, 3121 (1933).

[31] BALL AND CRANE, *ibid.*, **55**, 4860 (1933).

[32] (*a*) JONES AND GOSLIN, *ibid.*, **55**, 3500 (1933); (*b*) Ref. 28.

likewise have traced the localization of uranium salts in the organs of rabbits. Wissink[12g,h] has used this method for the detection of vitamin A.

PRESENT STATUS OF THE METHOD

During the past few years controversy has arisen, both as to the existence of time-lags in the Faraday effect and the reliability of the magneto-optic method of chemical analysis.

In support of the existence of a time-lag it is to be observed that all positive observations so far made may be interpreted as involving some kind of time factor. Allison and Condon[33] have observed that a mixture of compounds having positive and negative Verdet constants shows rotation in the Allison apparatus but not in a steady magnetic field. Allison, Christensen, and Waldo[34] have pointed out that minima cannot be explained on the basis of electrostatic effects, scattering, absorption, depolarization, transverse magnetic effects, phenomena characteristic of the magnetic field itself, poor contacts in the trolley system, or electrical influence. The same authors present the following in support of the hypothesis of time-lags. Minima are observed with (1) Nicols crossed and magnetic fields opposing, (2) Nicols uncrossed and magnetic fields assisting, (3) Nicols uncrossed at an angle not approaching $\pm 90°$ and magnetic fields opposing, and (4) with analyzing Nicol rotated in the direction of the magnetic rotation and magnetic fields assisting. Maxima are observed with (1) Nicols crossed and magnetic fields assisting, (2) Nicols uncrossed and magnetic fields opposing, and (3) analyzing Nicol rotated in the direction opposite to the magnetic rotation with the magnetic fields assisting. Maxima and minima coincide in every case.

The existence of time-lags has been questioned by Gravola[35] on the ground that the data of Allison[9] do not check with those of Beams and Allison.[8] Webb and Morey[36] have observed broad minima but have failed to find sharp minima of the Allison type. They attribute Allison's observations to some peculiar kind of Kerr effect. Farwell and Hawkes[37] have been unable to observe any consistent minima, and attribute Allison's results to physiological and psychological causes.

It is to be further observed that in solutions of such very small concentrations as are used in obtaining this effect it is hardly possible that sufficient rotation could be produced by the classical Faraday effect to account for the minima observed. An hypothesis of reaction times admirably explains the results obtained with the apparatus. Allison still holds that his results can only be accounted for in terms of a time-lag or a time of reaction in some phenomenon. In the light of numerous experiments designed to clarify the problem, he is led to believe that it is most probably a time-lag in some type of magnetic rotation, but not of the normal or classical Faraday type. This view is not universally accepted. Lack of an acceptable explanation for the Allison effect does not, however, invalidate the mass of experimental data which has been obtained on the magneto-optic apparatus.

Because of the extreme sensitivity reported for the magneto-optic method of chemical analysis, the many applications which have been made of it, and its seemingly unlimited possibilities as an aid in chemical research, the controversy has shifted from the question of time-lags to that concerning the very existence of minima and to the basis of the method, namely, whether minima are characteristic of the substances under observation.

Concerning the objectivity of the method the subject matter may be classified as follows: (1) the detection of positions of minima by observers from other laboratories on Allison's set-ups, (2) the observation of positions of minima in various laboratories, (3) the accuracy with which settings may be made, (4) the agreement with other methods of quantitative analysis, (5) the solution of unknowns, (6) the use of the photoelectric cell, and (7) the application of the photographic method.

The many publications from Allison's laboratory indicate that something capable of being reproduced objectively is under observation. Several persons have reported observing minima on Allison's apparatus. Yoe[23j] and Snoddy[23n] have observed the sixteen lead chloride minima. Yoe and Wingard[12c] have detected the formation of formaldehyde from carbon dioxide and water. Slack[38] has solved unknowns on Allison's apparatus although he believes he was unconsciously aided in some of the analyses. The authors have observed minima on Allison's two set-ups.

More conclusive, however, are the results obtained in laboratories in different parts of the country. McGhee and Lawrenz[17] have checked the results on element 87. Latimer and Young have confirmed the three minima of calcium[23h] and the two minima each of hydrochloric and hydrobromic acids.[21] These authors also report having checked a large number of Allison's minima. Ball and Cooper[23k] have shown that one of the minima previously attributed to nickel sulfate belongs to cobalt sulfate and have found a new minimum for nickel sulfate. They further pointed out that cobalt exhibited three minima instead of one in its compounds. The minima attributed previously to cobalt and nickel sulfates were confirmed. Ball and Crane[31] have observed the minima for pentavalent chromium which occur in that region of the scale predicted from Allison's data. Ball, Wulfkuehler, and Wingard have found evidence of the existence of trivalent tin chloride as an intermediate in the oxidation of stannous chloride with chromic

[33] ALLISON AND CONDON, *Phys. Rev.*, **40**, 1021 (1932).
[34] ALLISON, CHRISTENSEN, AND WALDO, *ibid.*, **40**, 1052 (1932).
[35] GRAVOLA, *ibid.*, **33**, 1033 (1929).
[36] WEBB AND MOREY, *ibid.*, **44**, 589 (1933).
[37] FARWELL AND HAWKES, *ibid.*, **47**, 78 (1935).
[38] SLACK, *J. Franklin Inst.*, **218**, 445 (1934).

acid.[39] Ball[40] has reported that in his laboratory about 300 of Allison's minima have been checked, and also has presented distribution curves showing that the positions of minima do not follow the law of chance.

In regard to the accuracy of setting upon minima positions, Allison,[9] in his earlier work, reported that the trolley setting for each minimum could be made within 0.20 scale division (3 cm.). More recently, since the technic of operation has been refined, several authors[41] have reported that minima positions can be reproduced within 0.01 to 0.03 scale divisions (1.5 to 4.5 mm.). When it is brought to mind that these settings were made in a dark room and that the observer had no knowledge of the actual trolley position other than that indicated by the occurrence of the minimum, the presence of minima and their reproduction seem to be confirmed.

As a further check on its validity the method has been developed quantitatively, and calcium[27a,b] has been determined within ten per cent. of the values obtained by permanganate titrations.

In the authors' opinion the successful solution of unknowns is one of the most convincing arguments; it definitely points to the existence of minima, and to the validity of the assumption that these minima are characteristic of the substance or substances under observation. McGhee and Lawrenz[17] have stated that twelve unknowns were given to Allison and his co-workers and that they were reported correctly within three hours. Slack[38] has announced that he has solved unknowns on Allison's set-up with approximately an eighty per cent. accuracy, but he believed he was unconsciously aided in some of the determinations. Recently Ball[40] has given an account of the solution of a series of unknowns by this method. He has reported that ten out of twelve unknowns have been determined correctly.

To meet the objection raised by many scientists that the minima read by the eye are purely subjective, attempts have been made to apply the photo-electric cell for the detection of minima. Allison, Christensen, and Waldo[42] have obtained positive results with the photo-electric cell. They report that by the galvanometer deflections produced by the amplified current, trolley positions were located which exactly coincided with those previously determined by the eye. They also report that the magnitudes of galvanometer deflection give an indication of the depth of the minimum, and that this depth changes slightly over wide variations in the concentration of the substance under observation. Wissink[12h] has used the photo-electric cell for the reading of minima in the detection of vitamin A.

The recent photographic work of Hughes and Goslin[43] is the most important research reported in support of the validity of the method. This work proves objectively the existence of minima. It shows further that minima determined visually are correct and that they are characteristic of the substances under observation. In this investigation the analyzing Nicol was replaced by a Wollaston prism, which permitted the reception of the polarized light emerging from the cells on a photographic plate in two spots. The Wollaston prism was rotated until the two spots were approximately of the same intensity (although no effort was made to balance them exactly) and a series of photographs was made for different trolley positions: (1) on that visually determined for a minimum and (2) off that position. This was done for several different compounds in aqueous solutions. Measurements were made of the density of the two spots on the developed plate in each case. Several hundred photographs[44] have been taken in four modes of operation, namely, with the current flowing in the direction of the Faraday rotation with fields both assisting and opposing, and with the current flowing in the direction opposite to the Faraday rotation with fields both assisting and opposing. In every case a difference in differential intensity of the two spots off and on a minimum position was determined. Not only was there a change in every case, but when the direction of the current was reversed, the differences reversed in sign. The differences in differential intensities ranged from three per cent. to ten per cent. depending chiefly on the mode of operation. The absolute change in intensity of light off and on a minimum position was found to be 0.7 per cent.

In contrast with the positive results cited above, several investigators have obtained negative results with the magneto-optic method. In particular these workers either have not observed sharp minima of the Allison type, or have found that, when observed, such minima could not be correlated with the trolley position or with the substance under observation. Papish[45] and his co-workers have reported that the method is inadequate. Slack[46] and Jeppesen and Bell[47] have found that the minima they observed could not be correlated with trolley position or with the substance under observation. Slack and Peoples,[46b] as well as Jeppesen and Bell,[47] have obtained minima both with and without the substance in the cell. MacPherson,[48] Webb and Morey,[36] and also Farwell and Hawkes[37] have been unable to obtain sharp minima of the Allison type. MacPherson[48b] has obtained negative results with the photographic method; he has reported,

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[39] BALL, WULFKUEHLER, AND WINGARD, *J. Am. Chem. Soc.*, **57**, 1729 (1935).
[40] BALL, *Phys. Rev.*, **47**, 548 (1935).
[41] Refs. 17; 23*h*, *j*, *k*; 31; 32*a*.
[42] ALLISON, CHRISTENSEN, AND WALDO, *Phys. Rev.*, **37**, 1003 (1931).
[43] HUGHES AND GOSLIN, *Phys. Rev.*, **47**, 317 (1935).
[44] Private communications.
[45] (*a*) PAPISH AND SHUMAN, *Science*, **74**, 636 (1931); (*b*) Ref. 18, p. 3818, footnote.
[46] (*a*) Ref. 38, p. 445; (*b*) SLACK AND PEOPLES, *Phys. Rev.*, **45**, 126 (1934).
[47] JEPPESEN AND BELL, *Phys. Rev.*, **47**, 546 (1935).
[48] (*a*) MACPHERSON, *ibid.*, **47**, 254 (1935); (*b*) **47**, 310 (1935).

however, that his method was accurate to changes in intensity of about three per cent., whereas repeated estimates[49] place the change in intensity off and on a minimum at about one per cent. and actual measurements by means of the photographic method place the change at 0.7 per cent. Webb and Morey[36] have obtained negative results with the photo-electric cell and have suggested that minima of the Allison type may be caused by a peculiar kind of Kerr effect characteristic of the Allison set-up.

[49] Private communications.

Slack[50] and Farwell and Hawkes[37] have attributed the presence of minima to physiological and psychological effects.

In the authors' opinion, a mass of positive data which has been confirmed by objective means far outweighs numerous negative results whether objectively or subjectively determined. The results obtained with the magneto-optic apparatus, therefore, have led the authors to believe conclusively that minima exist and that they are characteristic of the substance or substances under observation.

[50] Refs. 46*b*; 12*c*.

KO HUNG *on the* YELLOW *and the* WHITE

TENNEY L. DAVIS AND LU-CH'IANG WU

Massachusetts Institute of Technology, Cambridge, Massachusetts, and Sun Yatsen University, Canton, China

THE present paper is a survey of Ko Hung's chapter on the Yellow and the White (the sixteenth of the Inner Chapters of *Pao-p'u-tzu*), a translation* of which by Dr. Wu has recently been received from China. An account of Ko Hung himself (about 281–361 A.D.) and a discussion of his chapter on the Gold Medicine have been published in earlier numbers of THIS JOURNAL,[1] and a complete translation of the two chapters has been printed in the *Proceedings of the American Academy of Arts and Sciences*, **70**, 221–84 (1935).

The chapter on the Gold Medicine deals primarily with the preparation and effects of the pill of immortality, and that on the Yellow and the White primarily with the art of transmutation—but the two subjects are ultimately the same, for the pill of immortality in certain cases is clearly nothing else but the artificially produced noble metal resulting from the transmutatory process. The Gold Medicine is sometimes the pill of immortality itself, sometimes the product of the transmutation, and sometimes the reagent, the "powder of projection" or the "tincture" as the European alchemists called it, which accomplishes the conversion of the base to the noble metal. In the chapter on the Gold Medicine *Pao-p'u-tzu* describes the preparation of a certain medicine which has the power of imparting immortality to one who eats and drinks out of vessels which are made of it, from which it would appear that the medicine is simply actual gold. In the chapter on the Yellow and the White he discusses the eating of gold and silver for the attainment of immortality, kneadable gold, and the relative merits of the gold and silver which are found in nature as compared with those which are made by alchemy. Natural and artificial gold and silver are the same, but the *Tao-shih* are too poor to buy the natural metals and find it more convenient to prepare them.

The chapter on the Yellow and the White contains considerable autobiographical material. The author lists three books which he received from *Chêng Chün* and describes some of the conversations which he had with him concerning the principles of the art. He reports that *Chêng Chün* told him that he and *Tso Chün* had accomplished a successful compounding. He explains more fully his own attitude toward alchemy and his motives in writing about it. Although he has not been able to make gold and silver himself, he is sure of good results and has confidence in the truthfulness of his teachers.

> Most people ridicule me for my liking for things unorthodox. They take me to be queer for attempting to understand the incomprehensible. But why should I do so? Am I writing on these things just for the sake of leaving some works behind me when I am gone? But that is unnecessary, for my Outer Chapters and miscellaneous writings in two hundred volumes are quite enough to speak my mind to posterity. Moreover, in the Inner Chapters there are no rhetorical flourishes but mere plain outspoken words. I am also aware of the fact that the treatment of such matters will be looked upon by people of the world as being far-fetched. It is not comparable in the winning of popular appreciation to a treatment of the tangible affairs of the vulgar world. The reason why I do not refrain from writing on the subject, knowing that it will not be accorded proper reception by the world, is that I am sure of good results and of the truthfulness of my teachers.
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> On account of the poor facilities for communication in the land, and of my poverty, misfortune, and lack of means, I have not secured the necessary medicines for the compounding. Yet here I am telling people that I know how to make gold and

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[1] J. CHEM. EDUC., **11**, 517–20 (1934); **13**, 103–5 (1936).

silver while I myself remain poverty-stricken. Is this not like the case of a man who sells medicines for curing lameness while he himself cannot walk? How can people be expected to be convinced? However, such arguments are not infallible, and we may grant exceptions in certain cases. I work hard at weaving in black and white simply for the sake of interesting curious and truth-loving scholars of the future in the study of the *Tao*.

Many strange things occur in nature; why should not transmutation be possible?

Water and fire, which are in the sky, may be gotten by means of the *Yang Shui* (a light-concentrator of a copper alloy). *Ch'ien* (lead), which is white, can be reddened into *Tan* (red, redness, medicine). *Tan*, which is red, can be whitened into *Ch'ien*. . . .

Transformation is inherent in the nature of heaven and earth. Why then should we think that gold and silver cannot be made from other things? . . .

Narrow-minded and ignorant people take the profound to be uncouth, and relegate marvels to the realm of fiction. To these people anything that has not been spoken of by *Chou Kung* or Confucius, or is not to be found in the Classics, is untrue. Is this not narrow-mindedness and ignorance?

Pao-p'u-tzu tells a number of stories of workers who accomplished or tried to accomplish the compounding, and mentions the necessity for offerings and ceremonials, for isolation from evil and disturbing influences, and for other precautions.

Magistrate *Wu Ta Wên* of *Ch'êng Tu*, a learned and cultivated man, related that as a disciple of *Li Kên*, the *Tao-shih* (Seeker of the Way, Man of the Art), he saw him heating a mixture of *Ch'ien* (lead) and *Hsi* (tin). To this was added a pea-size quantity of medicine. Upon stirring with an iron ladle and cooling, silver was obtained. Having gotten the secret formula, *Wu Ta Wên* attempted the compounding himself. However, being an official in active service, he could not perform the one hundred day dieting and purification necessary for his success—and so ended in failure. And so he exclaimed that this world was not worth living in.

Huan Chün Shan relates the following: *Ch'êng Wei* of the *Han* dynasty had a liking for the art of the Yellow and the White. He married a lady from a *Tao-shih* family. Once *Wei* was commanded to serve his sovereign as a retainer on a trip. However he lacked appropriate attire for the occasion and was therefore deeply grieved. Thereupon his wife came to his help by uttering the incantation, "Pray send forth two measures of silk." Forthwith appeared the desired fabric.

One day *Wei* was attempting the compounding of the medicine according to the *Chên Chung Hung Pao* (The Great Treasure in the Pillow-Chest), a formula-book of *Huai-nan-tzu*, and was without success when his wife approached him and found him fanning a fire under a pot of quicksilver. She said, "Let me try my hand at it." With these words she sprinkled into the pot a small quantity of some medicine from a wallet. After a short while, silver was obtained. Highly astonished *Wei* demanded of his wife why hadn't she enlightened him on the *Tao*. She replied that the *Tao* was to be attained only by those who are especially blessed. Failing in his attempt to extract the desired information from his wife at the price of luxurious food and clothing, he tried by the advice of a friend to force her to yield the secret under the whip. Still the obdurate wife held her own, declaring that the *Tao* was to be revealed only to the appropriate persons. If they were the proper persons, the *Tao* would be revealed to them by the accomplished even if they were absolute strangers. If they were not of the right kind, they would not obtain the secrets of the *Tao* from the accomplished even by inflicting the penalty of piecemeal dissection of the body. But *Wei* kept on with his coercion until his wife ran about in madness with her body covered with mud and finally died. . . .

The conditions for compounding the Yellow and the White are similar to those for compounding the *Shên Tan* (Divine Medicine). More than a hundred days of dieting and purification are required. The formula-books should be thoroughly understood and then the suitable formulas should be chosen for execution. The compounding is beyond the vulgar, the uncleanly, and the untalented who aspire to magical proficiency. The methods should be learnt directly from the accomplished. The compounding should be done in clean places in mountainous recesses so as to keep vulgar fools in ignorance. *Liu Hsiang* tried the compounding in the palace with the help of courtiers. In that case the conditions of dieting, purification, and isolation were not fulfilled. How then could he be successful?

Pao-p'u-tzu's insistence upon the genuineness of the gold and silver of alchemy is especially important because of the light that it throws upon the difference between Chinese alchemy and Alexandrian chemistry. His discussion of make-believes shows that he was aware of the possibility of staining the metals and knew that the changes are only superficial and do not correspond to a real change of substance. The following passages set forth plainly the objectives of the Chinese alchemist in preparing real gold artificially for use as a medicine of immortality.

Once I queried *Chêng Chün* saying, "*Lao Chün* has put forth the maxim that no high value ought to be placed on precious things which are difficult to obtain. Now in time of peace and plenty gold is allowed to waste in the mountains and jades in the valleys. Why then should sages of old so value gold and silver as to leave behind them formulas for their making?" To this *Chêng Chün* replied, "*Lao Chün* was referring on the one hand to those who in their desperate effort to obtain gold to gratify their pleasure of appreciation and wasteful decoration and even to attain longevity would scan sands, break stones, tear down mountains, dry up deep waters, defy long distances and precipices and drowning, and go to other excesses to the detriment of people's useful work, and on the other hand to those profiteering business men who in their hot pursuit of wealth for the indulgence of their senses would do away with the virtues of faithfulness and fair play and risk their lives over waters and precipices. It is another story with the *Chên Jen* (Men of Truth, Men Proficient in the Art, Sages). For they make gold with the purpose, not of getting rich, but of becoming *Hsien* by eating it. Therefore it is written in the Book, 'Gold can be made wherewith people can be raised above this worldly life.' Silver may be eaten for similar ends but is not as effective as gold."

Then I asked further, "Why should we not eat the gold and silver which are already in existence instead of taking the trouble to make them? What are made will not be real gold and silver but just make-believes."

Said *Chêng Chün* in reply, "The gold and silver which are found in the world are suitable for the purpose. But *Tao-shih* are all poor; witness the adage that *Hsien* are never stout and *Tao-shih* never rich. *Tao-shih* usually go in groups of five or ten counting the teacher and his disciples. Poor as they are, how can they be expected to get the necessary gold and silver? Furthermore they cannot cover the great distances to gather the gold and silver which occur in nature. The only thing left for them to do is to make the metals themselves.

"In that they are the essences of the medicines, the gold and silver made are superior to those found in nature.

"Says the *Hsien Ching* (Book of Immortals), 'The refined spirit of *Tan* changes into gold.' This is the theory of the formation of gold from *Tan*. This is why gold is usually to be found underneath where *Tan* occurs.

"The gold obtained by successful compounding is uniform inside and out. It may be put through a hundred workings without suffering any change. Therefore it is written in the formulas for its making that it may be made into nails. That shows its

strength. Such results come of the responsive infusion of the *Tao* of nature. Why should such deeds be called make-believes?

"Make-believes should be like the besmearing of iron with *Tsêng Ch'ing* (a blue compound of copper), whereby the metal takes on a reddish sheen simulating copper, and the action of egg-white on silver to obtain a yellow coloring resembling gold. In all these cases there are merely external changes but no internal transformations."

Our author supports his argument by quotations from ancient authorities, The Jade Tablet Records, The Copper Pillar Book, The Inscriptions on the Tortoise Shells, etc. He points out that the secret names by which the substances are designated increase the difficulties, but gives what appear to be very straightforward descriptions of a number of processes many of which he ascribes to earlier authors and writings. Indeed he sometimes describes the apparatus and manipulation so clearly that a chemist nowadays could carry out the process if he knew what reagents to use.

The description of one process deserves special discussion, for it evidently concerns the preparation of stannic sulfide or "mosaic gold" and is perhaps the earliest known description of the preparation of this interesting substance. Mosaic gold exists in flakes or leaflets which have the color and luster of gold, it does not tarnish, and is used at present for bronzing radiators, gilding picture frames, and similar purposes. As *Ko Hung* describes the process, "According to the *Tso Huang Chin Fa* (Method of Gold Making) received by *Chin Lo Hsien Shêng* from *Ch'ing-lin-tzu*, tin sheets, each measuring six inches square by one and two-tenths inches thick, are covered with a one-tenth inch layer of a mud-like mixture of *Ch'ih Yen* (Red Salt) and *Huei Chih* (potash water, lime water), ten pounds of tin to every four of *Ch'ih Yen.*" They are then heated in a sealed earthenware pot for thirty days with horse manure (probably with a smouldering fire of horse manure). "All the tin becomes ash-like and interspersed with bean-like pieces which are the yellow gold." The large portion of the metallic tin is converted into some ash-like compound or possibly into the ash-like allotropic modification, gray tin. A small portion of the tin is converted into bean-size aggregates of flaky stannic sulfide. The yield is poor, for the author says that "twenty ounces of gold are obtained from every twenty pounds of tin used."

It seems likely that *Ko Hung* was personally experienced in the chemistry of tin, for the Chinese say that he was the first to make tin foil and that he made magic or spirit money out of it.

The Children's Method of Making Gold is described so fully that there seems reasonable hope of identifying the reagents and, in the future, of elucidating the chemistry of the process which evidently leads to a silver-like amalgam of some sort.

A large iron cylinder, one foot and two inches both in diameter and in height, and a small iron cylinder, six inches in diameter, are used. One pound of good powdered *Ch'ih Shih Chih* (talc?), one of *Hsiao Shih* (niter?), one of *Yün Mu* (mica?), one-half of *Liu* of *Huang* (sulfur), four ounces of *K'ung Ch'ing* (a blue copper compound?), and one of *Ning Shui Shih* (a mica-like mineral) are intimately ground together and passed through fine-meshed sieves. The paste obtained by mixing with vinegar is used to make a lining two-tenths of an inch thick on the inside of the small cylinder.

A mixture of one pound of mercury, one-half of *Tan Sha*, and one-half of *Liang Fei* is stirred thoroughly until the mercury has disappeared. It is then placed in the small cylinder, overlaid with *Yün Mu*, and covered with an iron lid. The *Liang Fei* is obtained as follows: To ten pounds of *Ch'ien* (lead) heated in an open iron pot over a furnace three ounces of mercury are added. The portion which comes out during the early stages of the operation is scooped off with an iron ladle and is called *Liang Fei*.

Molten lead is introduced into the large iron cylinder on a stove. The small cylinder with its contents is then placed in the large cylinder, its top one-half inch below that of the large one. Heat is applied to keep the lead molten. Strong heating is continued for three days and nights, when *Tzu Fen* (Purple Powder) will be obtained.

Silver is obtained by heating together mercury and *Tzu Fen* until they have attained very close relations and then pouring the material into water.

The latter part of the chapter describes a method for the softening of gold and details the effects which are produced by eating pills made from the kneadable material. By treating the pills in various ways and by applying them accordingly, other magical effects may be procured.

Upon treatment with *Mu Ching* wood and *Ch'ih Hsü Chiu* (a kind of alcoholic liquor) for a hundred days, the gold softens and becomes kneadable. The eating of one pound of this medicine in pills of the size of small beans, one pill at a time, three times a day, will kill off all the three worms and drive away all the hundred diseases. If the eater be a blind man, he will see; if a deaf man, he will hear; and if an old person, he will be rejuvenated to the state of thirty years of age. The eater will not be scorched by fire and will be invulnerable to all evils, poisons, bleak winds, and excessive heat and dampness.

The ingestion of three pounds will enable a person to walk on the surface of water. The hundred spirits of the mountains and waters will come to wait on him. He will live as long as heaven and earth. . . .

When a pill that is painted with the blood of a white goat is thrown into water, fishes and dragons will come forth to be caught.

A pill painted with the blood of a black goat, when hung over the gateway of a village, will protect the entire village from epidemics. If it is smeared on the foreheads of cattle, sheep, or any of the six domestic animals, they will be protected against diseases and against tigers and leopards. . . .

On putting a pill painted with *Li Yü Tan* (the carp's gall) into water, the water will go asunder making a gap of ten feet for breathing space. The carrying of such a pill will prevent one's clothes from being wetted in the rain. . . .

By carrying in one's hair a pill that has been boiled with *Tz'u Shih* one will be invulnerable in fighting against outlaws. All missiles directed at him will be reversed.

Compound *Liu Ting*, *Liu Jen*, and *Shang T'u* into a pill. When it is placed between the nose and the upper lip one's person will vanish from view. . . .

Inks prepared from such pills will penetrate stone, gold, and wood. The indentations will be too deep to be erased.

A person who has been dead for not more than a day may be revived by washing a pill down his throat and spraying his face with water of *Yüeh Chien Shang*.

By putting in his fingernail a pill that has been painted with wolf's and crane's blood, one can bring about changes in things by pointing his fingers at them and at the same time uttering verbal orders. The movement of mountains and trees may be

apparent to everybody when as a matter of fact no motion occurs.

The chapter ends with a general reference to the ceremonies which are necessary.

As in the case of the making of the nine medicines, services of worship should be properly performed to *T'ai I* (Supreme Monad), *Hsüan Nü*, and *Lao-tzu* in the making of the Yellow and the White. There should be constant burning of the five incenses. When gold is successfully compounded, three pounds of it should first be thrown into deep water and ten pounds of it in a marketplace before any of it is used for other purposes.

LU-CH'IANG WU

AFTER the proof of the present article had been read, a letter from China brought the sad news of the death of Dr. *Wu* on January 30, 1936, from typhoid, in the *Chung-Sun* hospital at *Canton*. This is a severe loss to scholarship. Dr. *Wu*'s translations from *Wei Po-yang*, from *Pao-p'u-tzu*, and from other Chinese sources have done more than the work of any other man to make available to the West the source materials of Chinese alchemy. They have supplied a basis for discussion, conjecture, and future study. They have made a real beginning of a job which will take long to finish, and have made possible the addition of a new chapter to our histories of chemistry.

LU-CH'IANG WU

Lu-Ch'iang Wu was born November 20, 1904, in *Kaiping, Kuangtung*, China, and received his early education in *Kueilin, Kuangsi*, and in *Canton*. He was the second son of *Ting-San Wu*, a learned man and president of the *Koa-Min* University in *Canton*. He graduated from *Tsing Hua* College, *Peiping*, in June, 1924, and was awarded scholarships, 1924–1929, for study in the United States. He came to the Massachusetts Institute of Technology, and in due course was awarded the Bachelor of Science degree in Chemical Engineering in 1928 and the Doctor of Philosophy degree in Organic Chemistry in 1931. He carried out the research for the Doctor's degree under the direction of the late Professor Samuel P. Mulliken on "The Generic Characterization of Ketones of Order I." During the last two years of his graduate study he undertook and completed the difficult task of translating into English the whole of the *Ts'an T'ung Ch'i* of *Wei Po-yang*. This work was written about 142 A.D., and is the earliest known treatise in any language which is devoted entirely to the subject of alchemy. *Wu*'s translation of it is the first translation of the whole of a Chinese alchemical treatise into a European language. During the same period he also translated a number of biographies from the *Lieh Hsien Ch'üan chuan* and an article on "The Origin and Evolution of the Doctrines of *Yin-yang* and *Wu-hsing*," by *Ch'i-Ch'ao Liang*, an article which throws much light upon the early development of Chinese scientific thought. The translations show a remarkable sense of English word values. Dr. *Wu* was widely read in English and was interested in the contemporary tendencies of Western philosophy. I have understood that he prepared a Chinese translation of one of the books of Bertrand Russell while he was a graduate student at M. I. T. The translation into English of the fourth and sixteenth chapters of *Pao-p'u-tzu* were made after his return to China.

After his return to China in 1931, Dr. *Wu* spent one year teaching chemistry at the National *Peking* University, and then joined the Chemical Engineering Department of *Sun Yatsen* University at *Canton* where he remained until the time of his death. Here he taught general chemistry, history of chemistry, biological chemistry, and food analysis. In 1933 he married *Ssu-Chuang Liang*, the second daughter of the distinguished scholar, *Ch'i-Ch'ao Liang*. She had graduated from McGill University and from the School of Library Service of Columbia University. A daughter survives him. At the time of his death he was engaged in translating Kruyt's textbook of colloid chemistry, and, with one of his students, in writing a textbook of inorganic chemistry in the Chinese language.

TENNEY L. DAVIS

LABORATORY METHOD *of* APPROACH *to* MODERN ACID-BASE THEORY

L. C. FLOWERS

Canal Zone Junior College, Balboa Heights, Canal Zone

A student laboratory experiment has proved of value in introducing the Lowry-Bronsted viewpoint on acids and bases to first-year students of general chemistry. Analogous titrations are carried out in glacial acetic acid and in aqueous solutions, end-points being determined by an indicator method.

✦ ✦ ✦ ✦ ✦ ✦

IN A NUMBER of recent papers stress has been laid on the need for a modernization of first-year courses in general chemistry. Among the topics considered due for a revision are the fundamental conceptions of acids and bases (*1, 2, 3, 4, 5*). All authors agree that we should introduce the Lowry-Brønsted ideas (*6, 7*) into our courses in an elementary way, redefining acids and bases in terms of their proton behavior. A simple and clear exposition of the modern view suitable for presentation to first-year students has recently been given by Dr. Kilpatrick (*5*).

During the past three years the writer has presented an elementary discussion of the newer ideas to his classes, introducing the subject shortly after a study of strong and weak electrolytes in which the electrical nature of ions and the dielectric behavior of the solvent is emphasized. Electronic explanations of salt formation have been given earlier in the year. In spite of this background many students seemed to experience considerable difficulty in assimilating the newer ideas. When analyzed, the difficulty seemed to be due primarily to a complete unfamiliarity with solvents other than water, and to an inability to reconcile the older treatment as given in the textbooks with the modern conceptions. To the student the orthodox explanations of acid-base equilibria, hydrolysis, etc., seemed adequate in dealing with the aqueous solutions to which his experience had been confined.

To remedy this situation an experimental method of approach was devised whereby the student would have some actual experience with non-aqueous solutions. The work is adapted either to lecture demonstration or to student laboratory procedure. Because of its success with his classes, the writer prefers the latter.

THE LABORATORY METHOD

The experimental details are quite simple. Solutions of sodium acetate, potassium acetate, and perchloric acid in glacial acetic acid are prepared in the stockroom and are made available to the student. The sodium acetate and perchloric acid solutions are of known and approximately equivalent concentrations. Aqueous solutions of sodium hydroxide, potassium hydroxide, sodium acetate, and perchloric acid are also prepared so as to be equivalent in molality to each other and to the acetic acid solutions. As indicators, two 0.1% solutions of basic fuchsin are used, one in glacial acetic, the other in aqueous solution.

The student is directed to titrate a 10-cc. portion of the solution of sodium acetate in acetic acid, using perchloric acid in the same solvent as the titrating acid. Two drops of indicator solution are used. He finds an endpoint when an equimolar quantity of the acid has been added; as the salt sodium perchlorate is soluble no precipitation occurs. He has been directed to use only dry equipment in this procedure so that it is clear to him that the hydroxyl ion is not a prerequisite to the "neutralization" of an acid. The point is made that the reaction has occurred because of the transfer of a proton (hydrogen ion) from the perchloric acid to the acetate ion furnished by the sodium acetate solution.

The concept of conjugate acids and bases and the fundamental definition can now be tied to a concrete example. $HClO_4$ is an acid splitting off a proton (H^+) from its conjugate base ClO_4^-. Acetate ion, Ac^-, is a base which accepts the proton, forming its conjugate acid, HAc. In both cases the reaction is of the type:

$$\textit{Acid} \rightleftharpoons \textit{Base} + H^+ \text{ (proton)}$$

in the first: $HClO_4 \rightleftharpoons ClO_4^- + H^+$

in the second: $HAc \rightleftharpoons Ac^- + H^+$

thus defining an acid and a base from the modern point of view. The student is asked to note that during the neutralization there exists a competition for protons between the base ClO_4^- and the base Ac^-, in which the Ac^- will win out, establishing it as a more basic ion than ClO_4^-. The result may be expressed by a double acid-base reaction:

$$\underset{\text{Acid (1)}}{HClO_4} + Na^+ + \underset{\text{Base (2)}}{Ac^-} \longrightarrow \underset{\text{Base (1)}}{ClO_4^-} + Na^+ + \underset{\text{Acid (2)}}{HAc}$$

in which the sodium ions take no part whatsoever. At the end-point the supply of Ac^- ions furnished with the sodium acetate solution is exhausted; remaining

in the acetic acid solution are the perchlorate and sodium ions, which are probably associated as ion-pairs owing to the low dielectric constant of acetic acid.

The titration is then duplicated with a glacial acetic acid solution of potassium acetate instead of sodium acetate. In this case the substance remaining after neutralization can be identified; potassium perchlorate precipitates as the neutralization progresses. This salt may be filtered off, washed and dried, and identified by the student. He is asked to interpret the reactions occurring during the titration and, as a general rule, succeeds very well. He readily understands that the positive ion (Na^+ or K^+) plays no part in the proton exchange reactions, that the acetate ion is the base rather than the sodium or potassium acetate, which substances are in reality salts.

The analogous behavior of aqueous solutions is now compared by having the student titrate 10-cc. portions of aqueous solutions of sodium hydroxide and potassium hydroxide with an aqueous solution of perchloric acid, using one cc. of a 0.1% aqueous solution of basic fuchsin as the indicator. As before, the sodium perchlorate remains in solution while potassium perchlorate precipitates. Here the competition for protons lies between the hydroxyl and perchlorate ions:

Acid	⇌	*Base*	+	H^+
$HClO_4$	⇌	ClO_4^-	+	H^+
H_2O	⇌	OH^-	+	H^+

in which the hydroxyl ion wins out, being a stronger base than ClO_4^-. The complete neutralization consists of a double acid-base reaction:

$$\underset{\text{Acid (1)}}{HClO_4} + M^+ + \underset{\text{Base (2)}}{OH^-} \longrightarrow \underset{\text{Base (1)}}{ClO_4^-} + M^+ + \underset{\text{Acid (2)}}{H_2O}$$

M^+ may be K^+ or Na^+, neither of which have anything to do with the fundamental acid-base reaction. Consequently the OH^- ion is the base, not the sodium hydroxide nor the potassium hydroxide, which are as truly salts as were the sodium and potassium acetates in the previous example.

It should now be possible to extend the theory to include the solvent. The aqueous solution of perchloric acid, being a good conductor of electricity, is known to be highly ionized. Either the perchloric acid is dissociated into ionic constituents or there is a reaction between it and the solvent water, resulting in the formation of ions. A simple dissociation of the perchloric acid would cause free protons to appear in the solution, a rather improbable occurrence, to say the least. Consequently, it must be supposed that a reaction does occur between the acid $HClO_4$ and the solvent H_2O. This reaction will be of the double acid-base type:

$$\underset{\text{Acid (1)}}{HClO_4} + \underset{\text{Base (2)}}{H_2O} \rightleftharpoons \underset{\text{Base (1)}}{ClO_4^-} + \underset{\text{Acid (2)}}{H_3O^+}$$

Again there is a competition for protons, this time between the ClO_4^- ions and the uncharged H_2O molecules, with H_2O being successful since it is more basic than the ClO_4^- ion. It is quite probable that a similar competition exists in the glacial acetic acid solution of perchloric acid:

$$HClO_4 + HAc \rightleftharpoons ClO_4^- + H_2Ac^+$$

However, the dielectric constant is so low in this case (about 10) that the ionic products must for the most part associate as ion-pairs, rather than lead an independent existence as ions.

In the cases studied, each neutralization is now seen to consist in reality of three reactions in which the added base, the solvent, and the conjugate base of the added acid compete for the possession of protons, the added base winning each contest. Thus in glacial acetic acid solution:

	Base	+	*proton*	⇌	*Acid*
(Added Base)	Ac^-	+	H^+	⇌	HAc
(Solvent)	HAc	+	H^+	⇌	H_2Ac^+
	ClO_4^-	+	H^+	⇌	$HClO_4$ (Added Acid),

in aqueous solution:

(Added Base)	OH^-	+	H^+	⇌	H_2O
(Solvent)	H_2O	+	H^+	⇌	H_3O^+
	ClO_4^-	+	H^+	⇌	$HClO_4$ (Added Acid),

and in general for an added base B, a solvent S, and an added acid, HX with conjugate base X, (*8*):

B	+	H^+	⇌	BH^+
S	+	H^+	⇌	SH^+
X	+	H^+	⇌	HX^+

where B and X may be ions of either sign, or may be uncharged molecules.

The student is now directed to add one cc. of aqueous basic fuchsin indicator to separate 10-cc. portions of aqueous solutions of sodium hydroxide and sodium acetate. The indicator will be decolorized in the hydroxide but not in the acetate solution. He is further directed to add aqueous perchloric acid to the hydroxide until the indicator color appears. This occurs at the endpoint, when the greater part of the OH^- ions have been removed by conversion to H_2O molecules. The OH^- ion is thus shown to be more basic in aqueous solution than the Ac^- ion, which failed to decolorize the indicator. In fact the Ac^- ion is only feebly basic in aqueous solution.

Of the three ions, ClO_4^-, Ac^-, and OH^-, ClO^-_4 has been shown as the least basic and OH^- as the most basic, Ac^- occupying a position somewhere between. Of the solvents, water is the more basic, since the acetate ion is less basic in this solvent than in glacial acetic acid. It has been the writer's experience that the student has his ideas on acids and bases clarified con-

siderably after following the above procedures and the accompanying explanations. Subsequent classroom discussions on solution equilibria were followed without difficulty.

EXPERIMENTAL DETAILS

1. Glacial Acetic Acid Solutions. Glacial acetic acid was selected as being probably the most satisfactory non-aqueous solvent, lending itself to a simple presentation of the points to be illustrated. It would have been desirable to use a solvent more basic, as well as one more acid than water, but no liquid suitable for the use of freshman students seemed available. The chemistry of glacial acetic acid solutions has been thoroughly investigated, particularly by Hall and Conant, (*8, 9*), Hall and Werner, (*10*), and Hall (*11*). A general review of the field has been given by Davidson (*12*). The writer feels greatly indebted to these investigators as his treatment of the subject is due mainly to their work.

2. Preparation of Acid. As suggested in the work of Hall and Conant (*8*), ordinary 99.5% glacial acetic acid is used with no attempt at dehydration. The perchloric acid solution is prepared according to Hall and Werner (*10*). The theoretical quantity of perchloric acid (60%) necessary to produce the desired concentration (the writer used molal solutions throughout the experiment) is added slowly to the calculated amount of chilled acetic anhydride. During this addition the mixture is shaken frequently and is kept in an ice bath. After the solution has been allowed to come to room temperature it will be found that the addition of a small quantity of either the 60% acid or the anhydride will cause a temperature rise. The constituent which does so is then added in small portions until no further temperature rise occurs, at which point the solution may be assumed to be non-aqueous and to contain no excess of anhydride. Glacial acetic acid is then added to produce a solution of the desired molality.

No danger will arise through the proper use of perchloric acid solutions of the concentrations given in this experiment. However, it is recommended that the dilution of the 60% acid be carried out by the instructor or by an experienced stockroom assistant. Students should also be warned of its violent action with reducing agents and cautioned against using it for any other purpose than that specified.

3. Preparation of Bases. Sodium acetate solution is prepared by adding a weighed quantity of sodium metal to glacial acetic acid, then diluting to the proper volume to produce the desired concentration. Or sufficient sodium metal may be added to produce a saturated solution of the acetate which is approximately 3.5 molal at 28°C. This solution may then be diluted to the proper concentration.

Owing to the greater reactivity of potassium metal no attempt has been made to weigh the metal so as to produce a solution of given concentration. Small pieces of the metal are added to glacial acetic acid, the molality of the resulting solution being adjusted by titration with the perchloric acid.

4. Preparation of Indicators. Dimethylamidoazobenzene, methyl orange, acid fuchsin, methyl violet, and basic fuchsin were investigated as possible indicators for the endpoints in titrations. The first three do not show a sufficiently sharp color transformation at the endpoint to be generally useful. Methyl orange may be of some educational value inasmuch as the student is already familiar with the "acid" and "basic" colors of the indicator, which appear respectively in the glacial acetic acid solutions of perchloric acid and sodium acetate to which it is added.

Methyl violet and basic fuchsin are, however, excellent indicators for titrations in glacial acetic acid, showing very sharp color changes at the endpoint. The color of methyl violet changes in rapid succession from a deep purple to blue to green to yellow with the addition of two drops of molar acid at the endpoint. It may be noted that methyl violet shows no such color change at the endpoint when aqueous solutions are titrated; instead there is a gradual shift from a deep purple to a blue as acid is added.

Since methyl violet is satisfactory it is to be expected that basic fuchsin should likewise show a sharp color transformation. The latter shows a marked change from magenta to a reddish yellow at the endpoint. While methyl violet cannot be used in aqueous solutions, basic fuchsin is satisfactory provided the bases are strong and the solutions are unbuffered. In water the magenta color is destroyed by strong bases but reappears as the base is neutralized, becoming permanent near the endpoint. Both methyl violet and basic fuchsin are readily soluble in glacial acetic acid, while methyl orange is only slightly soluble. Of the indicators mentioned basic fuchsin is preferred since it can be used in both glacial acetic and aqueous solutions, although it does not behave in the same manner in both solvents.

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EZRA STILES, ALCHEMIST *or* CHEMIST?

PHILIP E. BROWNING

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

EZRA STILES, seventh president of Yale College (1778–1795), was one of the most outstanding scholars of his day. His capacity for the acquisition of knowledge was truly amazing, and his famous diary, covering a period of a quarter of a century (1769–1795) contains a wealth of information about that period which is priceless in value. His almost daily comments on the weather have proved of great importance as they antedate by many years any official reports, and comparatively unimportant and incidental as they may have seemed to him at the time, they are very highly prized now.

In Stokes's "Eminent Yale Men," Vol. I, p. 307, we find the following note: "A century after his [Stiles] death, the author of the Literary History of the American Revolution referring to his liberal tendencies and wide interests says: 'A Universal Scholar,—He threw open every window of his mind, toward every quarter of the heavens and earth and came to have some claim, according to the standards of his time, to be called mathematician, astronomer, chemist, electrician, linguist, orientalist, antiquarian, meteorologist, jurist, theologian, Biblical translator and exegete.' "

We are not surprised then to find that Stiles was interested in the rather crude experimental work of his day, for to him it was just one of the avenues of knowledge which he felt impelled to investigate. Naturally the vocabulary he used was that of his contemporaries.

The following entries from his diary* indicate some of his alchemistic-chemical interests and activities:

July 18, 1777. Hodie finivi Perlectiones Bibliothecae chemicae ab Albines editae.

Aug. 16, 1777. Terra sol. Aethere sublata hodie.

Aug. 22, 1777. Expt of Ebullition of Aether with Solution of silver in Aqua fortis.

Dec. 1, 1785. In Even'g I attended Mr. Jones's chemical Lecture. He says within a year or two it has been discovered that Spt. of sea salt drawn over a Semi Metal becomes a Solvent of Gold, Silver and all other Metals. He gave me a Quantity of Vitriolic AEther.

Dec. 7, 1785. This Even'g I attended the Chemical Lect. and saw Turpeth Min and red precip made by combin'g spt. Nit. and Vitr. with Mercury. Tho't of first imbid'g aether then decant'g it off, then affus'g it to sp. Nitr. and then etc.

Dec. 15, 19, and 22, 1785. Attended Chemical Lecture.

Mar. 19, 1789. Thursday Mr. Woodruff visited me and shewed me a sample of (a silver like substance) made about the middle of last Dec. by Eben Cahoon aet 25.

Aug. 13, 1792. This day Dr. AEneas Munson shewed me a Piece of malleable whitish Metal, which he himself made within a Month past. It was fixt. Mercury, the first I ever saw.

Aug. 30, 1792. Dr. AEneas Munson shewed me another piece of Mercury which he had fixt indeed but not malleable. He told me that Capt. Phipps last year was shown the Exper't at Savanna by a Dr. Prentice thus—Phipps melted Lead and when so far cold as to begin to grow hard, but while yet hot he Phipps poured upon the congeal'g Lead, Mercury, which then became fixt by the fumes of the Lead. The Dr. then told him to melt the first substance and gave him a small portion of grey Powder about a pinch of Snuff wc. Phipps took and cast on the Metal or Mercury in fusion, and it coold and fixt. The Dr. told him it would break in hammering unless etc. and gave him some corrosive sublimate. He melted it again, cast on the sublimate, and it became malleable.

Another Man told Dr. Munson he himself had by Dr. Prentice's Direction treated four Ounces of Mercury in the same manner, and made it also p'fect Silver with the loss of a few Grams only. . . .

Stiles' interest in science continued throughout his

PENCIL SKETCH OF PRESIDENT STILES BY ST. JOHN HONEYWOOD (1780)

* "The Literary Diary of Ezra Stiles," edited by FRANKLIN B. DEXTER, Chas. Scribner's Sons, New York City, 1901, and Yale University Press.

These entries are given in their original form with the spelling and abbreviations as nearly identical with the published edition as possible.

life. He died May 12, 1795, in his 68th year. An entry in his diary, April 16, 1795, states that he attended Meigs' lecture on Natural Philosophy on that date.

Although Stiles found this alchemistic form of experimentation of interest, the following entries show that his keen mind was not misled by false interpretations of the phenomena which he saw and heard described.

July 1, 1777. Interspersed among my miscellaneous Writings may be found Things respecting the Rosacrucian Philosophy, which may induce some to imagine that I have more Knowledge of that matter than I really have. I have no Knowledge of it at all; I never saw Transmutation, the aurific Powder nor the Philosopher's Stone; nor did I ever converse with an Adept knowing him to be such. The only man that I ever suspected as a real and true Adept was Rabbi Tobias of Poland, but he evaded my Interrogaturies and communicated to me nothing—I believe he was only a conjectural speculative Philosopher. I have known 2 or 3 Persons (as Judge Danforth and Rev. Mr. West) who believed in the reality of the philosopher's Stone, but neither of them ever obtained it. They are only conjectural and speculative Philosophers—and of such Dr. Franklin told me there were several in Philada etc who were loosing their time in chemical Experiments of no effect. I never saw or made an Expt. with a furnace or Alembic in all my Life. I am not versed in the Books of the Adepts; I have seen but few of those Authors and read less—perhaps all I have collected would not equal a common Octavo Volume. I am infinitely less acquainted with that than other of the Sciences in the whole Encyclopaedia of Literature. I never absorbed the extracted Sulpher of Gold in Terra—I have no practical Knowledge of the Matter; the few Ideas I have about it are only imaginary, conjectural and speculative. Coram Deo Veritas.

March 3, 1789. Dr. — visited me again to-day to converse about the Transmuta'. of Metals, which he says Dr. Koon p'formed at Wallingford last Dec. He is infatuated with the Notion that I know something about it. I told him I knew nothing but what was in the Books, that I never had possessed the Secret if there was any that I never saw or conversed with any one that I thought had it, that I never performed Transmutation or seen it p'formed; and that I held the whole to be a vain and delusory Pursuit.

That which however appeals most strongly to us in this tercentenary year* of our chemical industries is the intelligent and far-seeing interest he showed in the development of the chemical industries of his time.

The following entries, made almost at the central point of time between the beginnings with John Winthrop the younger in 1635 and the present day, cannot fail to be of interest.

July 24, 1777. At Berwick last week I saw a manufactory of Copperas lately set up there by Col. Chadburn. He shewed me in a Keeler some of the Copperas as it had just been set aside for chrystallizing. The Rocks and Stones are found in great Plenty in Lebanon about 8 or 10 M off. A man at York bro't home 6 or 7 pounds of stone, and powder'g it dissolved it in water and boiling it down the Chrystals formed and weighed a pound. Upon this Applica'. was made to the Colonel to be at the Expense of buying Kettles etc. But he having a Saltpetre Work, offered them that for the present. Thereupon the Men carted a Load of Rock thither and are now breaking and soaking it and boiling down the impregnated Water. The Copperas is excellent.

Sept. 22, 1777. It is wonderfully ordered in divine Providence that so many Things should conspire toward establishing the Independ'y of America. Heavens open Resourses and Supplies within ourselves. The Discovery of our being able to make Saltpetre and Copperas lately, as well as Potash formerly, and these in great Abundance is of this kind. And now that our W. India Supplies are cut off, Heaven has led us to the successful experiment on Corn stalks, from whence it is probable may be made an abund't Supply of Molasses and Rum for this whole Continent. This is done with only the Topping of the corn without damaging the ear or Grain. In Old York 8M. from Portsm'o are erected last week two Mills, consisting of 3 plane Wooden Cylinders with the Improv't of Coggs atop. In these Mills they have already made some considerable Molasses from Corn Tops—and some of the Molasses has been distilled into good Rum. It is said the Produce is at the rate of two Bbs. Molasses to an acre of Corn. Suppose a good acre producing 25 or 30 Bushels Corn, then for every dozen Bush. Corn, we may reckon a Bb. Molasses; but reckon it 1 Bb. to 30 Bushels. There may be 150 Th. Fam'ys in N. England consuming 30 Bush. each annually for the pple. and Cattle. And as there are nearer 200 Th. Families the Total annual Consumption and Expenditure of Grain in N. Engld. will be 5 or six Millions of Bushels—the produce of England I think is about forty Million Bushels; and Old Engld. contains about six times as many Inhab. as N. Engld. Of the Grain raised in N. Engld. more than one half is Indian—the Total of which may be ann'y 3 Mill Bushels, the Corn Tops of which will produce 100 Th. Bbs. Molasses if we reckon 2 Bbs. of 30 Bush. or the produce of a good acre, it will be 200 Th. Bbs. An amazing Discovery. A Supply of 1 Bb. to a family with ease. The whole Continental Import'a from the W. Indies never equald this. There was a prospect of our Depend'a on the W. Ind. increasing with our Popul'a and Demand of Rum and Molasses and Sugar, and the price increasing. The W. Indian planters counted upon the erroneous Rise of the price of Tropical Produce; and this would have most assuredly proved the case, had not Heaven opened Resourses among ourselves. It is probable Corn Tops will furnish an ample supply of both Spirits and Molasses, phps. Sugar. We can bear to be depend't on the W. Ind for the latter, as we can pay in Lumber. I believe the Cane will grow in the So. States.

Nov. 14, 1777. At Middletown, Ten Thousd. Gallons of Stalk Juice delivered in this fall to one distillery which distilled near a Thousd. Gall. of good Rum. Ordinary Ratio twelve Gall. Juice yield one Gall. Spt. or Rum.

June 1, 1787. Mr. Erkelens visited me, full of his Cobalt Mine and China Voyage. He some years ago bought the Governor's Ring, as it is called, or a Mountain in the N.W. corner of East Haddam, comprehend'g about 800 acres or about a sq. mile area. Here he finds plenty of Cobalt, which he manufactures into Smalt with which is made beautiful Blue on china Ware. One Ton of Ore is manufact. into eighteen viz. 1 part Ore, 3 pts Flints and 3 pts. potash—and repeating this on the Regulus. The smalt is worth 2/ster p pound in Holland brot from China. But at 1/ it will become 100 p. Ton Ore becomes £ 1800 sterl'g.

Gov. Trumbull has often told me that this was the place to which Gov. Winthrop of N. Lond. used to resort with his Servant; and after spend'g three Weeks in the Woods of this Mountain in roast'g Ores and assaying Metals and casting gold Rings, he used to return home to N. London with plenty of Gold. Hence this is called the Gov. Winthrop's Ring to this day. Gov. Winthrop was an Adept, in intimate Correspond. with Sir. Knelm Digby and first chemical and philosophical Character of the last Century as may be seen in the Dedic'a of 40th Vol. Phil. Transactions 1740.

Mr. Erkelens about 1775 being a Projector, erected a Distillery in Had. 6M fr. Middlet'o on a stream decend's from this Mountain—he also purchased the Cobalt Mine there. He had been at £ 2000/ster Expense to no profit. He is going on a voyage to China carrying with him 20 Tons Cobalt Ore.

From a study of the foregoing material we may conclude that Stiles could hardly be classed among the alchemists of his time, and according to our present-day standards, he would hardly qualify as a chemist.

* The manuscript of this note was prepared in the summer of 1935; poverty of space has delayed publication until now.

We may, however, I feel sure, justly place him among the chemists of his generation and certainly among those who looked forward with prophetic interest to the development of the chemical industries of his native land.

The following extracts from Abiel Holmes' "Life of President Stiles," published in 1798, show Stiles's further interests in scientific and industrial developments:

Page 102. In 1763 he commenced a course of chemical experiments which he continued for several succeeding years.

Page 103. Dr. Franklin having lately presented him with a Fahrenheit thermometer, on the first of January (1763) he began a series of thermometric and meteorological observations, which he continued, with very little interruption, with his own hand, till within two days of his death. These observations were made with frequency in the course of the day, and especially when there was any remarkable variation in the temperature of heat or cold, or any phenomena relating to meteorology. They compose a rich treasure in this article of science; and are contained in six quarto volumes.

He now (1763) commenced experiments for the raising of silk worms and for the culture of silk: and wrote letters abroad to obtain information on the subject from the silk manufactories. He kept a journal, in which he interspersed remarks selected from the various authors on the silk culture, particularly after the Italien and Chinese manner: and as he continued to make experiments, and, with great assiduity, to invite the attention of the community to the subject for a series of years, his journal, collectively, constitutes a quarto volume.

Page 306 (1789). Convinced, by observation and experiments, that the culture of silk might be carried on with success and profit in New England, he this year took great pains for the extensive distribution of mulberry feed, as the first step toward this manufacture. He sent an estimated quantity of feed to eighty ministers in Connecticut, with a printed circular letter, desiring them, by themselves or by such persons as they might employ in their parishes, to sow each a nursery of 4000 trees in a parish, on this condition, That, at the end of three years, three quarters of the trees, then living, belong to the planters, and one quarter to be distributed gratis in the respective parishes.

ANOMALOUS VALENCES *of the* RARE EARTHS*

D. W. PEARCE†

Department of Chemistry, University of Illinois, Urbana, Illinois

AND P. W. SELWOOD

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

All the rare earths commonly have a valence of three. Cerium, praseodymium, terbium, and possibly dysprosium may also be quadrivalent, while samarium, europium, ytterbium, and probably thulium may be divalent. The interpretation of anomalous valence in terms of electronic configuration has been attempted through the use of pertinent magnetic and optical data, and an explanation is offered for the distinct periodicity of valence exhibited within the rare earth group. Advantage of the anomalous valences has been taken in suggested new analytical and separation methods.

✦ ✦ ✦ ✦ ✦ ✦

ALL THE rare-earth elements commonly exhibit a valence of three, and they are properly placed together as one element in the third group of the Periodic Table as shown in Figure 1 (*1*). This arrangement also indicates a certain periodicity within the rare earth group, the significance of which will appear later. But it has been known for a long time that cerium, praseodymium, and terbium also have a valence

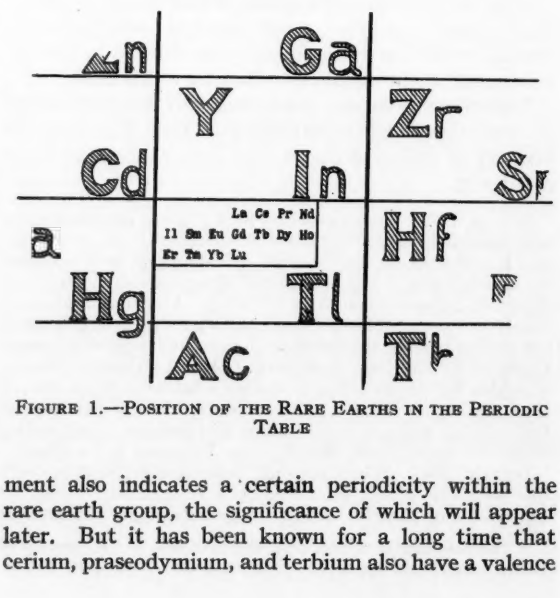


FIGURE 1.—POSITION OF THE RARE EARTHS IN THE PERIODIC TABLE

* Contribution to the symposium on Recent Advances in the Chemistry of the Rarer Elements, conducted by the Division of Physical and Inorganic Chemistry at the eighty-ninth meeting of the American Chemical Society, New York, April 25, 1935.

† Now Instructor in Chemistry, Purdue University, West Lafayette, Indiana.

of four, and that samarium and europium can have a valence of two. Some writers have used these deviations from trivalence as an excuse for spreading the rare earths out across the Periodic Table, so that we find, say, neodymium in such strange company as that of manganese. Such attempts, however, do nothing but betray a misunderstanding as to both the chemistry and atomic structure of these elements. The Mendeléeff table has been an extraordinarily useful generalization, but no service is done by ignoring its several deficiencies, one of which is that there is only a single place for all fifteen rare earths. The questions that now arise are: can these anomalous valences be interpreted in terms of electronic structure? Can predictions be made as to hitherto undiscovered examples of non-trivalence? And what unique and useful properties are possessed by rare earths in these anomalous valence states?

ATOMIC STRUCTURE

Table 1 shows the distribution of electrons among the various energy levels of the rare-earth elements. All the levels up to the $4f$ are filled. The $5s$ and $5p$ are also filled, while the two $5d$ electrons and one $6s$ electron are those lost in formation of the normal trivalent ion. In going from a rare-earth element to the one of next higher atomic number, the additional electron is added, not to the outside of the atom, but to the $4f$ shell where it is to a considerable extent shielded from external influence. As is well-known, this shielding is responsible for the marked similarity of chemical properties throughout the rare-earth group.

TABLE 1

ARRANGEMENT OF ELECTRONS IN THE RARE EARTHS

	Lower levels all filled	$4f$	$5s$	$5p$	$5d$	$6s$
La		0	2	6	2	1
Ce		1	2	6	2	1
Pr		2	2	6	2	1
Nd		3	2	6	2	1
Il		4	2	6	2	1
Sm		5	2	6	2	1
Eu		6	2	6	2	
Gd		7	2	6	2	1
Tb		8	2	6	2	1
Dy		9	2	6	2	1
Ho		10	2	6	2	1
Er		11	2	6	2	1
Tm		12	2	6	2	1
Yb		13	2	6	2	1
Lu		14	2	6	2	1

Examination of this table will show that formation of a quadrivalent from a trivalent ion might be brought about, not by elimination of one of the $5p$ electrons, but rather by removal of one of the $4f$ electrons. On the other hand, in the formation of a divalent ion the remaining $5d$ electron might slip back into the $4f$ shell. In this way the electronic configuration of a quadrivalent ion would be identical with that trivalent ion immediately preceding it, while the configuration of a divalent ion would be identical with that of the trivalent ion immediately following it. An attempt will be made to show, in what follows, that this is precisely what does happen.

No property of the rare earths is of more general interest than their magnetic susceptibilities. This is because this property is peculiarly amenable to theoretical treatment, and it *is* so for the same reason that the *chemical* properties of these elements are so similar. In general the paramagnetism of an ion is made up of two parts, first that part contributed by the orbital motion of the unpaired electrons, and second that part contributed by the spin of the unpaired electrons. In most ions the spin component is not appreciably influenced by external conditions, although the orbital component is often largely if not completely quenched by the surrounding crystal field or field of oriented solvent dipoles. But in the rare earths, the $4f$ electrons, which are responsible for their paramagnetism, are sufficiently well protected so that only a little quenching of the orbital moment takes place (*2*).

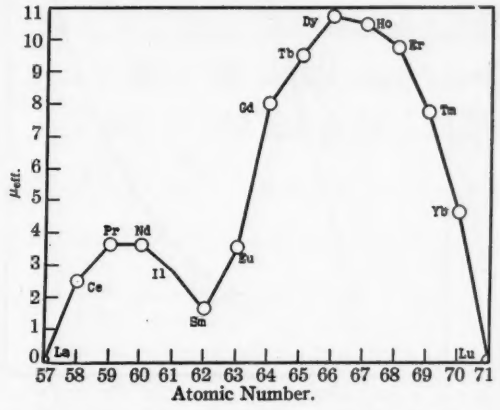


FIGURE 2.—EFFECTIVE BOHR MAGNETON NUMBERS OF THE RARE-EARTH TRIVALENT IONS AT ROOM TEMPERATURE

Now suppose attention is concentrated on the trivalent ion of gadolinium. Here is an ion which on good grounds is believed to have no orbital component of magnetic moment at all. In other words it has no multiplet structure; its normal state is ^8S. The magnetic susceptibility of most substances may be represented by the Weiss Law $\chi = C/(T + \Delta)$. The molecular field constant Δ is, in part, a measure of the degree of quenching of the orbital moment, so that if gadolinium really has no orbital moment, then Δ should be zero. This is precisely the case for a compound such as gadolinium sulfate octahydrate. Now divalent europium has the same number of electrons as trivalent gadolinium. Table 2 shows how the magnetic susceptibilities of these two substances compare. Not only are the magnetic susceptibilities almost equal but the molecular field constants are also very nearly equal. No ion other than one in an S state could have such a low value for Δ. The electronic configuration of the divalent europium ion must therefore be identical with that of the trivalent gadolinium ion (*3*, *4*).

TABLE 2

MAGNETIC SUSCEPTIBILITIES AND CURIE CONSTANTS OF DIVALENT EUROPIUM AND TRIVALENT GADOLINIUM

Temp. °K.	$\chi_{Eu} \times 10^6$	$\chi_{Gd} \times 10^6$	$\chi_{Eu}(T+4)$	$\chi_{Gd}(T+2)$
343	22020	23500	7.64	8.11
293	23800	27500	7.66	8.11
223	33650	35900	7.64	8.09
153	48500	52100	7.62	8.08
83	87700	95200	7.63	8.10

The susceptibility of the trivalent europium ion at 293°C. is about 5000 × 10^6, only one-fifth as great as the above. The molecular field constant Δ is subject to an error of about ±2.

A similar situation exists with respect to the isoelectronic pair, divalent samarium and trivalent europium (*5*). Figure 3 shows effective Bohr magneton

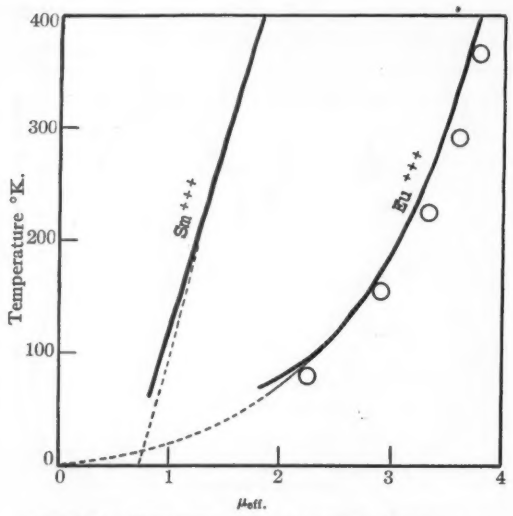


FIGURE 3.—EFFECTIVE BOHR MAGNETON NUMBERS FOR THE IONS Sm^{+++}, Eu^{+++}, Sm^{++}: EXPERIMENTAL POINTS ○ ARE FOR Sm^{++}

numbers of these two ions plotted against absolute temperature. The solid lines are for the trivalent ions of samarium and europium, while the experimental points are for divalent samarium. The dotted lines indicate theoretical extension of the data to absolute zero. In this case it is not possible to determine the molecular field constant with any degree of accuracy, and it is doubtful if it would have any significance even if obtained. But in view of the correspondence at all temperatures investigated, it is probably safe to say that the electronic configurations of these two ions are also identical. The arrangement of electrons in trivalent europium from the $4f$ shell out is $4f^6\ 5s^2\ 5p^6$. In divalent samarium it is probably the $6s$ and one of the $5d$ electrons which are lost. The remaining $5d$ electron does not, however, remain in that position but migrates back to the $4f$ shell. Its ready removal again is attested by the extremely easy oxidation $Sm^{++} \rightarrow Sm^{+++} + e$. Similarly with respect to other isoelectronic pairs, it is found that to a first approximation:

$\chi_{Ce^{++++}} = \chi_{La^{+++}}$, $\chi_{Pr^{++++}} = \chi_{Ce^{+++}}$, $\chi_{Tb^{++++}} = \chi_{Gd^{+++}}$, and $\chi_{Yb^{++}} = \chi_{Lu^{+++}}$

These relations do not, of course, hold exactly, and especially in the case of samarium and europium it is perhaps a little surprising that the correspondence is as good as it is, because both these elements have decidedly anomalous temperature coefficients of magnetic susceptibility.

Table 3 shows all the known valence states of all the rare earths arranged so that ions with equal numbers of electrons are on the same row. The table also indicates the normal spectral terms probably associated with each ion together with the number of $4f$ electrons present. These spectral terms were originally assigned to the trivalent ions only. It has now been shown that they are equally applicable to the divalent ions of samarium and europium, and most likely to the other non-trivalent ions indicated.

The capacity of certain rare earths to form non-trivalent ions is readily seen from this table to consist in a tendency to reach the normal condition of lanthanum, gadolinium, or lutecium. To be sure, in some cases the ion is not able to go all the way and this condition is characterized by intense color and chemical instability. The question now arises: what characteristic of the normal states of lanthanum, gadolinium, and lutecium accounts for this tendency? The answer must obviously be that these three elements alone are in S states; they have no multiplet structure; the orbital component of magnetic moment in each is lacking.

On the basis of this consideration, Klemm (*6*) was able some years ago to predict the existence of divalent ytterbium. Another possibility concerns thulium. It will be noticed that thulium stands in precisely the same relationship to ytterbium that samarium bears to europium. It might be expected, therefore, that

TABLE 3

ISOELECTRONIC ARRANGEMENT OF THE RARE-EARTH IONS

No. of Electrons	*Term*	*Divalent*	*Trivalent*	*Quadrivalent*
54	$4f^0\ ^1S$		La^{+++}	Ce^{++++}
55	$4f^1\ ^2F_{5/2}$		Ce^{+++}	Pr^{++++}
56	$4f^2\ ^3H_4$		Pr^{+++}	
57	$4f^3\ ^4I_{9/2}$		Nd^{+++}	
58	$4f^4\ ^5I_4$....		Il^{+++}	
59	$4f^5\ ^6H_{5/2}$....		Sm^{+++}	
60	$4f^6\ ^7F_0$....	Sm^{++}	Eu^{+++}	
61	$4f^7\ ^8S$	Eu^{++}	Gd^{+++}	Tb^{++++}
62	$4f^8\ ^7F_6$		Tb^{+++}	
63	$4f^9\ ^6H_{15/2}$		Dy^{+++}	
64	$4f^{10}\ ^5I_8$		Ho^{+++}	
65	$4f^{11}\ ^4I_{15/2}$		Er^{+++}	
66	$4f^{12}\ ^3H_6$		Tm^{+++}	
67	$4f^{13}\ ^2F_{7/2}$	?	Yb^{+++}	
68	$4f^{14}\ ^1S$	Yb^{++}	Lu^{+++}	

thulium would form a series of intensely colored, unstable, divalent compounds analogous to those of samarium. So far no direct evidence has been adduced to show that this is the case. There is, however, some reason to believe that divalent thulium has a transitory existence during the reduction of anhydrous

thulium trichloride to the metal (*7*). There would also appear to be a possibility of dysprosium forming an unstable quadrivalent oxide analogous to that of praseodymium, but of this there is no evidence whatever.

Next to their paramagnetism no property of the rare earths has awakened more interest than have their absorption spectra. The compounds of these elements exhibit a beautiful range of colors, and they are nearly all rich in sharply defined absorption bands in the visible or ultraviolet. As first pointed out by Main Smith (*8*), the rare earths show a sequence of color in that the colors of the first seven normal ions are similar to those of the last seven taken in reverse order.

TABLE 4

COLOR SEQUENCE IN THE RARE EARTHS

Trivalent Ions	*Color*	*Non-trivalent Ions*
La^{+++}	Colorless	Ce^{++++} (red)
Ce	Colorless	Pr^{++++}(black)
Pr	Green	
Nd	Red	
Il	Yellow ?	
Sm	Yellow	Sm^{++} (brown)
Eu	Faint pink	Eu^{++} (colorless)
Gd	Colorless	
Tb	Faint pink	Tb^{++++} (brown)
Dy	Yellow	
Ho	Yellow	
Er	Red	
Tm	Green	
Yb	Colorless	Yb^{++} (green)
Lu	Colorless	

The origin of color of rare-earth compounds is a complicated question and one which is still far from solution. It is known, however, that the 4*f* electrons, those responsible for paramagnetism, are also responsible for the color, and it might be expected that ions with the same numbers of electrons would show the same color. But such is by no means the case. Quadrivalent praseodymium is black instead of colorless, divalent samarium is brown instead of pink. One is inclined to believe that the often intense color of non-trivalent rare-earth compounds is a property of the molecule rather than of the ion. For instance, ceric cerium shows a range of color in different compounds from yellow to intense red. Not much has been done on the absorption spectra of non-trivalent compounds. However, we do know that the reflection spectrum of solid samarium dibromide consists only of a diffuse band throughout the visible region, and that divalent ytterbium has none of the discrete bands characteristic of most trivalent rare-earth salts.

Apart from ceric cerium, comparatively little is known about other properties of non-trivalent rare-earth compounds, but a recent letter in *Nature* (*9*) pointed out that divalent compounds of both europium and ytterbium exhibit a strong blue fluorescence when exposed to ultraviolet light. The fluorescence is similar to that observed in the mineral fluorite, and it has been suggested that the minute traces of europium present in fluorite, together with other rare earths, may be responsible for the well-known effect in the mineral.

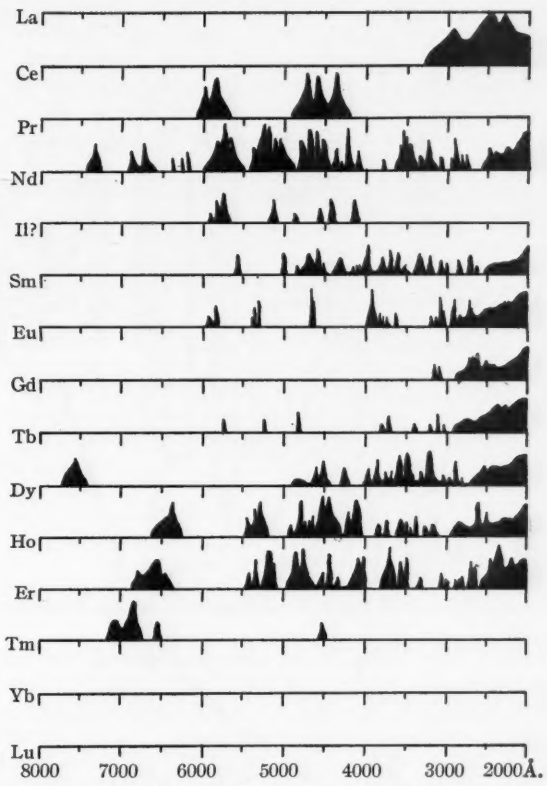


FIGURE 4.—ABSORPTION SPECTRA OF THE RARE EARTHS

[Taken mostly from PRANDTL AND SCHEINER, *Z. anorg. allgem. Chem.*, **220**, 107 (1934). The ordinates are a measure of log equivalent thickness through which the bands are visible.]

PREPARATION AND CHEMICAL REACTIONS

The higher oxides of cerium, praseodymium, and terbium may be prepared by ignition of their oxalates, carbonates, or nitrates. Oxidation of praseodymium and terbium is incomplete unless the material is fused with an alkali nitrate or else in an atmosphere of oxygen. A great deal of discussion is to be found in the literature with regard to the formulas of the oxides obtained when praseodymium and terbium materials are ignited in air. In some of these cases it seems likely that salt-like compounds are formed, similar, say, to lead plumbate. Quadrivalent praseodymium and terbium are found only in the form of the oxides.

Quadrivalent cerium may also be formed in other ways, such as by oxidation with hydrogen peroxide, chlorine, or potassium permanganate, or by the anodic oxidation process of Neckers and Kremers (*10*). As ceric phosphate is insoluble in acid solution, this forms one of the well-known separation methods for removing cerium from its neighbors.

In general, there are three methods available for the preparation of divalent rare-earth compounds. These are, first, high temperature reduction of the anhydrous

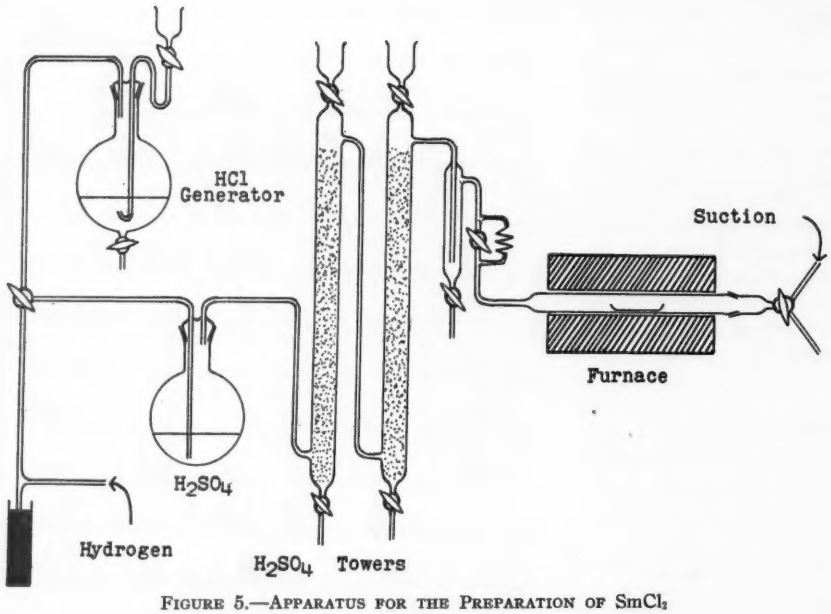


FIGURE 5.—APPARATUS FOR THE PREPARATION OF $SmCl_2$

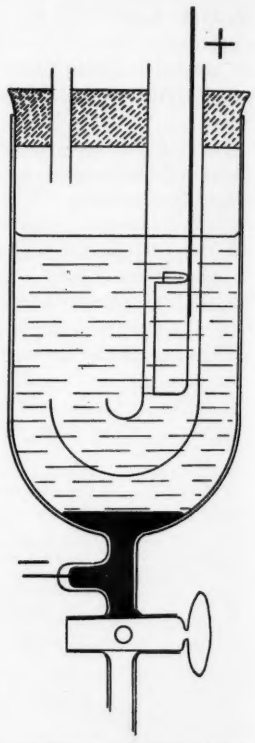


FIGURE 6.—ELECTROLYTIC CELL FOR THE PREPARATION OF $EuSO_4$ AND $YbSO_4$

halides with hydrogen or ammonia; second, thermal decomposition of the tri-iodides; and third, electrolytic reduction of the trivalent ion in the presence of sulfate, with consequent precipitation of the divalent sulfate.

In the case of samarium, electrolytic reduction is not available because divalent samarium reacts rapidly with water; in fact samarium dichloride quickly decomposes even on exposure to moist air. An example of the high-temperature hydrogen reduction is to be found in the following preparation of samarium dichloride: the preparation consists of two steps, first, dehydration of the moist trichloride, and second, reduction with hydrogen to the dichloride. Both these steps may conveniently be carried out in the same apparatus. (Figure 5.) A stream of hydrogen chloride gas is dried over sulfuric acid and passed over the hydrated trichloride at a pressure of a few centimeters of mercury. The temperature is held for two hours at 90°, an hour at 130°, and is then slowly raised to 250°, when dehydration is complete. The resultant product should be both anhydrous and quite free from basic contamination. Pure, dry hydrogen at normal pressure is then passed over the salt while the temperature is slowly raised to 740° and held there for five hours. Progress of reduction can be followed by development of the intense chocolate-brown color characteristic of divalent samarium. Completion of reaction is indicated by discontinued evolution of hydrogen chloride. The product, on analysis for both samarium and chlorine, is found to run in different batches from 50% to 90% pure $SmCl_2$, the remainder being unreduced $SmCl_3$.

Divalent europium and ytterbium compounds may readily be prepared by analogous methods, but these substances are much more stable than those containing divalent samarium, and for them electrolytic reduction has much in its favor. The fact that trivalent europium could be reduced electrolytically at the surface of a mercury cathode was discovered by Yntema (*11*) in 1930. In the presence of sulfate ion, $EuSO_4$ is precipitated and, after being washed with water, alcohol, and ether, is found to be practically free from any other rare earth. The electrolytic cell shown in Figure 6 is Prandtl's modification of Yntema's cell, having an internal anode and being so simple as to require no further explanation. W. E. Pearce, also at the University of Illinois, has found it possible to reduce europium by sifting into its water solution powdered magnesium, aluminum, or iron. Negative results were obtained by the use of such reducing agents as stannous chloride or ferrous sulfate.

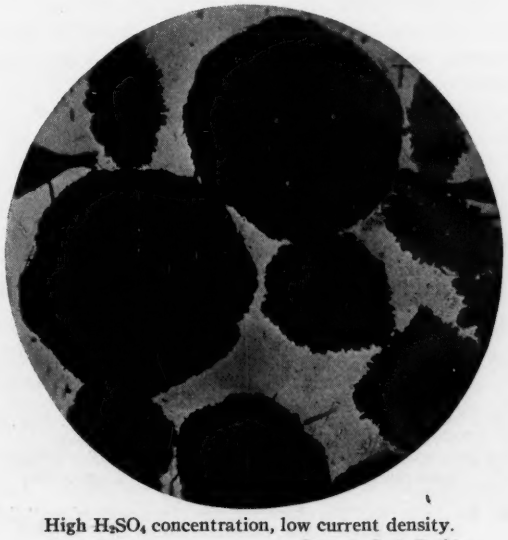
The electrolytic method has been extended by Ball and Yntema (*12*) to the preparation of divalent ytterbium sulfate, and has been used by Prandtl for the preparation of atomic-weight ytterbium. Divalent ytterbium sulfate reacts rapidly with sulfuric acid as soon as the current is turned off. Nevertheless, the optima conditions for its precipitation are obtained when solutions 0.2 *N* in Yb and 1.2 *N* in H_2SO_4 are electrolyzed at a current density of 0.08 amperes per square cm. When these are used a granular precipitate composed of spherical particles is formed. Lower acidity or higher current density, or both, result in the formation of finely crystalline material—presumably due to the more rapid reduction and precipitation. The formation of granular material causes no greater

inclusion of impurities from the mother-liquor, a fact established by spectroscopic evidence (*13*).

The granular precipitate (Figure 7) shows much less reactivity toward acid than do the acicular crystals obtained under less ideal conditions. This effect is not merely a matter of surface area, but is apparently also due to the fact, proved by photomicrographs, that the surfaces of the spherical particles are composed of the terminal faces of the acicular crystals, On these faces the rate of wastage is low because of the strong crystallization forces acting in these directions (*14*).

The method, which is fractional, inasmuch as it removes only part of the ytterbium at each run, enables the preparation of thulium, ytterbium, and lutecium oxides of very high purity. Spectroscopic evidence showed the purity of the ytterbium to be 99.9% and the thulium and lutecium to be between 97% and 98%.

Low H_2SO_4 concentration, high current density.



High H_2SO_4 concentration, low current density.

Courtesy, B. S. Hopkins

FIGURE 7.—PHOTOMICROGRAPHS OF CRYSTALLINE $YbSO_4$

The several types of reactions undergone by rare-earth compounds are shown in Table 5. The reactions shown by equations 1, 2, and 3 take place when the dihalides are allowed to stand in contact with air or water. Reactions 4 and 5 are general for divalent halides and are most rapid for the iodides. Equation 6 represents the reaction of the rare-earth metal (produced, say, in equation 5) with the silica of a porcelain boat. If metallic boats (*e. g.*, gold or platinum) are used, small amounts of the rare-earth metal alloy may be obtained. The reaction of a divalent sulfate with sulfuric acid is indicated in equation 7, and the precipitation of a divalent sulfate in equation 8. Divalent rare-earth chromates and phosphates are also insoluble in water.

TABLE 5

REACTIONS OF DIVALENT RARE-EARTH COMPOUNDS

1. $2RCl_2 + 2H_2O \rightarrow 2ROCl + 3HCl + H_2$
2. $6RCl_2 + 3H_2O \rightarrow 4RCl_3 + R_2O_3 + 3H_2$
3. $12RCl_2 + 3O_2 \rightarrow 4RCl_3 + R_2O_3$
4. $2RI_2 \rightarrow 2RI_3 + I_2$
5. $3RI_2 \rightarrow 2RI_3 + R$
6. $4R + 3SiO_2 \rightarrow 2R_2O_3 + 3Si$
7. $2RSO_4 + H_2SO_4 \rightarrow R_2(SO_4)_3 + H_2$
8. $RCl_2 + H_2SO_4 \rightarrow RSO_4 + 2HCl$

APPLICATION TO ANALYTICAL AND SEPARATION METHODS

Especially where intense color changes are found, compounds of non-trivalent rare earths would appear to have an analytical application. This is particularly true in the attempted detection of small amounts of one rare earth present as impurity in another. One such application has been known for a long time in the standard qualitative procedures for cerium. Addition of ammonium hydroxide to a solution containing cerium in the presence of hydrogen peroxide results in the intense and extremely sensitive orange coloration characteristic of quadrivalent cerium.

Other possible tests such as those involving the higher oxides of praseodymium and terbium have been used from time to time. About one per cent. of the former element present in lanthanum, cerium, or neodymium is sufficient to give the oxide a brown or gray tint provided ignition is done with good access to air. Similarly, small amounts of terbium in gadolinium are detectable by the same procedure. Terbium in dysprosium is less readily detected because dysprosium oxide itself has a buff tint.

The presence of samarium (*15*) in neodymium, europium, or gadolinium may readily be shown by treatment of the anhydrous mixed halides with hydrogen at about 700°C. The intense brown color of divalent samarium compounds is sensitive to about 0.1 per cent. and is not interfered with by other possible impurities. In such a test europium, if present, will also be reduced, but divalent europium is colorless. This method for samarium is more sensitive than the absorption spectrum and compares favorably with the arc or

spark spectrum without requiring fairly extensive spectrographic equipment.

In the cases of europium and ytterbium, a few per cent. of either of these elements may be indicated by formation of the divalent sulfate on electrolytic reduction of the solution. This method is especially valuable for ytterbium which has no characteristic absorption spectrum. Somewhat smaller amounts of ytterbium may be detected by the green color developed in the electrolytic bath, even though no precipitate is actually formed. However, these chemical tests for europium and ytterbium cannot compare in sensitivity with the remarkably intense and persistent arc or spark spectrum.

The extraordinary difficulty and tediousness of rare-earth separations has, of course, been due to the great similarity of these elements in the normal valence states, and heretofore separations such as fractional crystallization have been carried out under conditions such that all the elements present were in the trivalent condition. The late Professor James, of the University of New Hampshire, conducted, over a period of years, some ten thousand operations in order to prepare a few grams of pure thulium oxide. In connection with the present active interest in hydrogen isotopes, it may be pointed out that the labor involved in the preparation of heavy water is only a drop in the bucket compared with the extraction of any but the commonest members of the rare-earth group. Utilization of the anomalous valences would appear to offer great possibilities in improving the general rare-earth separation methods.

Until comparatively recently, quantitative procedures in the rare-earth field have been limited to the separation of cerium from its neighbors. The late Professor Brauner (*16*) of Prague has, however, obtained a good separation of praseodymium, especially from lanthanum, by fusion with alkali nitrates at high temperatures, and the work of Yntema, and of Ball and Yntema has extended quantitative separations to europium and to ytterbium. But even so, because of the small quantities of these elements found in rare-earth mixtures, it has still been necessary to resort to fractional crystallization over a period of a year or more before the reduction method became applicable.

An attempt has recently been made to facilitate the separation of europium through the use of a co-precipitant (*17*). In a mixture of terbium earths too dilute in europium to give any precipitate of $EuSO_4$ it has been found that the presence of barium sulfate, formed by the addition to the electrolytic bath of a dilute chloride solution, results in the substantial, if not complete, co-precipitation of all the europium present. The europium is then readily recovered from the filtered barium sulfate by washing it repeatedly with a little hot concentrated nitric acid. There seems no reason, therefore, why europium, and for that matter ytterbium also, cannot be removed practically quantitatively from a crude rare-earth mixture in as many days as it formerly took years.

There is an added advantage in the accumulation of quantities of pure ytterbium. This element may then be used as a "separating element," in analogy to the well-known use of bismuth, to effect the slow but quantitative resolution of thulium and lutecium, which has always been a separation of extraordinary difficulty.

A possible separation of neodymium and samarium has also been investigated. The mixture of anhydrous chlorides is treated with hydrogen at 700°C. This results in reduction of the samarium to the dichloride. On treatment of the resultant mixture with water, the reaction is one of those previously indicated, the samarium goes partly to trichloride and partly to insoluble oxide, while the neodymium chloride simply dissolves. Part of the samarium is precipitated, but seems always to be contaminated with some neodymium. Although the separation obtained is good, as rare-earth separations go, it is nevertheless only fractional, and because of its difficulty probably cannot compete with the usual double nitrate fractional crystallization.

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LIQUID AMMONIA RESEARCH IN 1935—A REVIEW

NORMAN O. CAPPEL AND GEORGE W. WATT*

The Ohio State University, Columbus, Ohio

IN PRESENTING this brief account of recent researches involving liquid ammonia, many instances have arisen in which current work either duplicates or is very closely related to work previously reviewed. In such cases, the writers have adopted the policy of referring the reader to earlier papers in this series (*1*, *2*) from which additional information and primary references may be obtained.

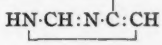
Many instances may be cited in which the discovery or development of a useful experimental method or technic has long antedated its general acceptance and application to the solution of a wide variety of problems. Such has been the case with liquid ammonia. Undoubtedly, this situation may, in part, be attributed to the fact that many workers have been inclined to overemphasize the experimental difficulties involved in the use of liquified gases as solvents. Of recent years, however, there has been a growing tendency toward the more general utilization of the unusual solvent properties of liquid ammonia. This has been most noticeable in the field of organic chemistry, as may be seen by reference to many of the original papers discussed in the following pages.

An extensive investigation of reactions of amino acids and related compounds in liquid ammonia has been carried out by du Vigneaud and co-workers. They have prepared β-alanine in almost quantitative yields by the reduction of *N*-carbobenzoxy-β-alanine with sodium in liquid ammonia at -33.4°C. (*3*).

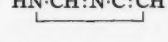
$$C_6H_5CH_2OCONHCH_2CH_2CO_2H + Na \text{ (slight excess)} \longrightarrow NH_2CH_2CH_2CO_2H + C_6H_5CH_2CH_2C_6H_5.$$

Other products of the reaction indicated above were not identified. In a similar manner, carnosine was prepared in 80% yield from carbobenzoxycarnosine,

$$C_6H_5CH_2OCONHCH_2CH_2CONHCH(CO_2H)CH_2 + Na \longrightarrow$$



$$NH_2CH_2CH_2CONHCH(CO_2H)CH_2$$



The reduction of inactive homocystine by means of a slight excess of sodium in liquid ammonia at -77°C. has been shown to result in the production of the sodium salt which, when treated with benzyl chloride reacts to form a 95% yield of *dl*-*S*-benzylhomocysteine (*4*),

$$[HO_2CCH(NH_2)CH_2CH_2]_2S_2 + 2Na \longrightarrow 2NaSCH_2CH_2CH(NH_2)CO_2H + 2C_6H_5CH_2Cl \longrightarrow 2C_6H_5CH_2SCH_2CH_2CH(NH_2)CO_2H + NaCl$$

d-Homocystine was obtained in 75% yields from *S*-benzyl-*d*-homocysteine by reduction with a slight excess of sodium in liquid ammonia, followed by oxidation of the resulting sodium homocysteinate,

$$2C_6H_5CH_2SCH_2CH_2CH(NH_2)CO_2H + 2Na \longrightarrow NaSCH_2CH_2CH(NH_2)CO_2Na$$

$$\xrightarrow[H_2O]{[O]} [HO_2CCH(NH_2)CH_2CH_2]_2S_2$$

Crystalline homocysteine has been isolated in 80% yields by the reduction of *S*-benzylhomocysteine, followed by acidification of the sodium salt formed in the reduction reaction (*5*). Homocystine has been converted to methionine in liquid ammonia by the reduction of homocystine with a slight excess of sodium followed by methylation with methyl iodide (*6*),

$$[HO_2CCH(NH_2)CH_2CH_2]_2S_2 + 2Na \longrightarrow 2HO_2CCH(NH_2)CH_2CH_2SNa + 2CH_3I \longrightarrow 2HO_2CCH(NH_2)CH_2CH_2SCH_3$$

In a similar manner, homomethionine has been prepared in 80% yields from pentocystine, (*7*),

$$[HO_2CCH(NH_2)CH_2CH_2CH_2]_2S_2 + 2Na \longrightarrow 2HO_2CCH(NH_2)CH_2CH_2CH_2SNa + 2CH_3I \longrightarrow 2HO_2CCH(NH_2)CH_2CH_2CH_2SCH_3$$

S-benzyl pentocysteine has been prepared by the reduction of pentocystine with sodium in liquid ammonia followed by the reaction of benzyl chloride with the sodium salt formed in the reduction reaction. From *S*-benzyl homocysteine, a 75% yield of homocystine was obtained by reduction with sodium in liquid ammonia followed by acidification and oxidation of the reduction product (*8*). Dibenzyl and toluene have been identified as products of the reduction reaction. The application of reactions of the type discussed above to the synthesis of dipeptides derived from cystine, cysteine, and glycine, has been studied by Loring and du Vigneaud (*9*).

The ammonolysis of the ethyl ester of *N*-carbobenzoxy-*d*-glutaminic acid has been found to result in the formation of the ammonium salt of *N*-carbobenzoxy-*d*-glutamic acid amide (*10*),

$$C_2H_5OCOCH_2CH_2CHCO_2H \quad (C_6H_5CH_2OCONH) + 2NH_3 \longrightarrow NH_2COCH_2CH_2CHCO_2NH_4 \quad (C_6H_5CH_2OCONH) + C_2H_5OH$$

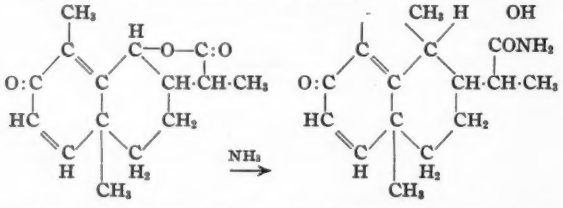
The reaction was effected by treating the ester with liquid ammonia in a sealed tube for 24 hours at 15–20°C. The action of liquid ammonia on cellobiose

* Present address: The Goodyear Tire & Rubber Co., Akron, Ohio.

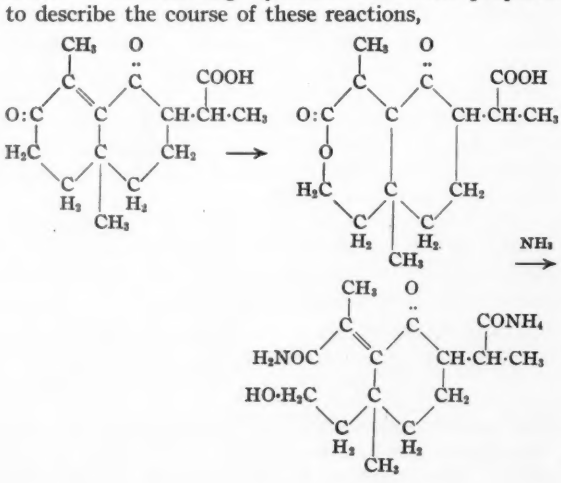
octaacetate in a sealed tube at 50°C. has been shown to result in the formation of ammonium acetate and a product which, when reacetylated, gave a peracetate containing nitrogen (*11*). An earlier review (*2*) referred to a preliminary announcement of the complete methylation of isosucrose. This work has since been described in detail (*12*). The methylation was accomplished by treating the potassium salt of heptamethylisosucrose in liquid ammonia, at its boiling point, with methyl iodide.

Fluorene and 9-iminofluorene have been identified as products of the interaction of dibiphenyleneethylene and liquid ammonia (*13*). A period of three weeks was allowed for completion of the reaction, which was carried out in a sealed tube at 65°C. The preparation of pure 9,10-dihydroanthracene in 76% yield by the reduction of anthracene with sodium in liquid ammonia at its boiling point has been reported (*14*). The respective solubilities of anthracene, phenanthrene, and carbazole in 100 grams of liquid ammonia have been found to be 0.8, 3.0, and 7.0 grams respectively at 40°, and 0.5, 5.5, and 12.5 grams at 20°C. (*15*). On the basis of this information, a partial purification of anthracene has been accomplished by washing crude anthracene with liquid ammonia.

A quantitative yield of the amide of santonic acid has been obtained by Abkin and Medvedev (*16*) by the ammonolysis of santonin with liquid ammonia in a sealed tube at room temperature.



Under similar conditions, the lactone derived from santonic acid has been shown to react with ammonia to form the ammonium salt of a dicarboxylic acid amide. The following equations have been proposed to describe the course of these reactions,



Bachman (*17*) has found that the bromo- and dibromoölefins, 1-bromopropene-1, 1-bromoöctene-1, 1,1-dibromopropene-1, and 1,1-dibromoöctene-1, are reduced by solutions of sodium in liquid ammonia at −33°C. to the corresponding acetylenes and olefins. The formation of relatively large quantities of high molecular weight polymers also resulted from the reduction of the dibromoölefins. The dibromo compounds gave higher yields of acetylenes than did the monosubstituted olefins, and in both cases the yields of acetylenes increased with increase in the length of the hydrocarbon chain.

Vaughn and Danehy (*18*) have prepared a number of acetylenes by means of reactions between alkyl halides or sulfates and calcium acetylide in liquid ammonia. Calcium acetylide was prepared either by passing acetylene into solutions of calcium in liquid ammonia or by adding solutions of calcium to solutions of acetylene. The reaction between diethyl sulfate and calcium acetylide has been shown to result in a theoretical yield of pure 1-butyne, while reactions with amyl chloride, amyl bromide, and butyl bromide produced the corresponding acetylenes in yields of 56%, 31%, and 45%, respectively.

Hauser and Jordan (*19*) have shown that the reactions which occur between acetyl-α-aldoximes and potassium amide in liquid ammonia may be represented by the general equations,

$$RCH{:}NO(OCCH_3) + KNH_2 \longrightarrow RCN + CH_3CO_2K + NH_3$$
$$RCH{:}NO(OCCH_3) + KNH_2 \longrightarrow RCH{:}NOK + CH_3CONH_2$$

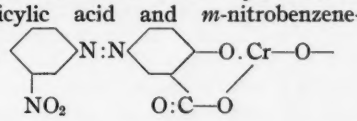
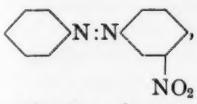
Comparatively high yields of nitrile lead to the conclusion that the rate of the first of the above reactions is greater than that of the ammonolytic reaction which produces the potassium salt of the oxime. Similarly, Hauser and co-workers (*20*) have shown that analogous reactions of carbethoxy-α-benzaldoximes result in high yields of nitrile and low yields of oxime. Apparently these reactions were carried out in open Dewar tubes at the boiling point of ammonia.

The action of liquid ammonia at its boiling point on 2-(4-bromobenzoyl)benzoyl chloride has been shown to result in a 95% yield of the corresponding acid amide (*21*),

$$BrC_6H_4COC_6H_4COCl + 2NH_3 \longrightarrow BrC_6H_4COC_6H_4CONH_2 + NH_4Cl$$

The application of the classical Williamson reaction to the preparation of simple and mixed ethers in liquid ammonia at 1 to 10 atmospheres pressure and at temperatures above the normal boiling point of ammonia, has been investigated (*22*). Ethers containing from six to eleven carbon atoms were prepared in yields ranging from 3–45%. Alkyl bromides were found to be more satisfactory than the corresponding chlorides or iodides, the former being relatively unreactive, and the iodides too readily ammonolyzed through interaction with the solvent. These and earlier studies have led to the generalization that, in any process involving the reaction of an alkyl halide in liquid ammonia with a sodium compound that is

decomposable by water, the formation of appreciable quantities of ethers will result unless the reactions are effected under strictly anhydrous conditions.

A hydrated chromium salt of the azo dye obtained by coupling salicylic acid and *m*-nitrobenzenediazoniumchloride,  ,  , $2H_2O$, has been shown to add two molecules of ammonia when treated with liquid ammonia at temperatures in the neighborhood of −70°C. (*23*). It is believed that the ammonia molecules are coördinately bound to the chromium atom.

Bolotov and Popova (*24*) have described their work on the preparation of urea from carbon dioxide and liquid ammonia. Urea was produced in 50–60% yields by heating the two reactants in an autoclave for one and one-half hours at 175–85°C., and at 150–75 atmospheres pressure. Davis and co-workers (*25*) have shown that the synthesis of urea from ammonium carbamate may be accomplished during the ammoniation of peat.

Evidence in support of the view that metal ketyls such as sodium and potassium benzophenone contain a carbon-metal bond has been presented by Wooster and Dean (*26*). They have shown that diphenylethoxymethyl-sodium may be prepared in liquid ammonia at its boiling point by the cleavage of benzophenone diethyl acetal,

$$(C_6H_5)_2C(OC_2H_5)_2 + 2Na \longrightarrow (C_6H_5)_2C(Na)OC_2H_5 + C_2H_5ONa,$$

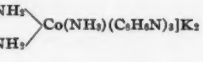
and that the corresponding potassium compound results from the action of potassium amide on benzhydryl ethyl ether,

$$(C_6H_5)_2CHOC_2H_5 + KNH_2 \longrightarrow (C_6H_5)_2C(K)OC_2H_5 + NH_3.$$

Studies of the stability of the alkali compounds so produced, determination of the ethoxyl content of the products obtained by the reactions of the metal ketyls and ethyl bromide, and a study of the reaction between triphenylmethyl and sodium benzophenone, have been described.

The formation of complex pyrrole and indole salts of cobalt, nickel, iron, and chromium in liquid ammonia at room temperature has been reported (*27*). These salts were prepared by the action of the potassium salts of pyrrole and indole on ammonated halides of the above metals. Potassium pyrrole and hexamminoferrous chloride, $Fe(NH_3)_6Cl_2$, react to form the complex salt, $[(C_4H_4N)_4Fe]K_2$. The indole complexes prepared are listed in Table 1.

TABLE 1

Salt	*Indole Complex*
$Ni(NH_3)_6SO_4$	$(C_8H_6N)_4NiK_2$
$[Cr(NH_3)_5Cl]Cl_2$	$(NH_3)_2Cr(NH_2)(C_8H_6N)_2K$
$Co(NH_3)_6SO_4$	$(C_8H_6N)_2Co(NH_2)K$
$Co(NH_3)_6Cl_3$	

The potassium salts of pyrrole and indole used in this investigation were prepared by the action of potassium amide on pyrrole and indole in liquid ammonia.

It has been observed that thallium triethyl is unreactive toward liquid ammonia (*28*).

The reduction of zirconium bromide with an excess of potassium in liquid ammonia at or near its boiling point has been found to result in the formation of an ammonate of the potassium salt of zirconium imide, $Zr(NK)_2 \cdot NH_3$ (*29*). The same product was formed when the halide reacted with an excess of potassium amide, while an equivalent quantity of potassium amide produced an equimolecular mixture of zirconium imide, $Zr(NH)_2$, and its monopotassium salt, Zr(NH)NK. Thorium bromide was not *reduced* by potassium, but did react to form a product, $Th(NH)NK \cdot NH_3$, analogous to that formed by the reduction of zirconium bromide and the subsequent reaction of the reduction products. An excess of potassium amide reacted with thorium bromide with the formation of the molecular compound, $Th(NK)_2 \cdot KNH_2$. A study of the system thorium bromide–ammonia at 0° and 25°C. and at pressures up to 1190 mm. has provided evidence for the existence of the ammines listed in Table 2 (*30*). The approximate decomposition pressures were determined graphically from the pressure-composition diagram.

TABLE 2

Temp. (°C.)	*Ammine*	*Approximate Decomp. Pressure (Mm.)*
0	$ThBr_4 \cdot 20NH_3$	1180
0	$ThBr_4 \cdot 18NH_3$	268
0	$ThBr_4 \cdot 10NH_3$	22
25	$ThBr_4 \cdot 10NH_3$	184

It is of interest to compare these data with results obtained by Chauvenet (*31*), which indicate that, under comparable conditions, the ammine of highest ammonia content formed by thorium chloride is the compound, $ThCl_4 \cdot 18NH_3$.

Mono- and disilane have been prepared in 70–80% yields by the action of magnesium silicide on a solution of ammonium bromide in liquid ammonia at −33°C. (*32*). Monosilane, SiH_4, was found to be the principal reaction product. The formation of disilane, Si_2H_6, depends upon the temperature at which the reaction is effected and upon the composition of the silicide used. It has been shown that a silicide prepared at or near 500°C. yields very pure monosilane, while silicides prepared at higher temperatures (not exceeding 1000°C.) yield appreciable quantities of disilane.

Moureu and Rocquet (*33*, *2*) have extended their studies of the reaction between phosphorus pentachloride and liquid ammonia. They have found that the initial reaction product, $P(NH_2)_5$, cannot be isolated. It is believed to dissociate at 0°C. and pressures below 300 mm. with the formation of a material having a composition represented by the formula, PN_3H_4, which was shown to be a mixture of $(PN_3H_4)_4$ and $(PN_3H_4)_3$. These substances decomposed to form $(PN_2H)_n$.

$$PCl_5 + 8NH_3 \longrightarrow 5NH_4Cl + PN_3H_4 + 2NH_3$$
$$PN_3H_4 \longrightarrow (PN_3H_4)_4 + (PN_3H_4)_3 \longrightarrow (PN_2H)_n + NH_3$$

The ammonolysis of tantalum pentachloride (*34*) at the boiling point of liquid ammonia has been shown to occur in accordance with the equation,

$$TaCl_5 + 17NH_3 \longrightarrow Ta(NH_2)_2Cl_3 \cdot 7NH_3 + 2NH_4Cl \cdot 3NH_3.$$

Tantalum nitride, TaN, may be prepared by the thermal decomposition of the above product.

Schwarz and Striebich (*35*) have found that the solubility of bismuth halides in liquid ammonia increases with increasing atomic weight of the anion. These halides are not *ammonolyzed* by liquid ammonia, but form rather well-defined series of ammonates which may be divided into two classes, addition and intercalated compounds, having molecular and ionic lattices, respectively. $BiCl_3$ forms ammonates with 0.5, 1.0, and 12.5 moles of NH_3 per mole of salt; $BiBr_3$ with 0.5, 1.5, 3.0, 14.0, and 18.5 NH_3; BiI_3 with 2.0, 3.0, 4.0, 8.0 (?), 12.0, 12.5, 16.0, 18.5, and 22.0 NH_3.

Smeets (*36*) has reported that ammonates of barium perchlorate, $Ba(ClO_4)_2 x NH_3$, where $x = 2, 5, 6$, or 9, are soluble in liquid ammonia.

Carbonyls of lithium, rubidium, and calcium have been prepared by Pearson (*37*) by the action of dry carbon monoxide on liquid ammonia solutions of the metals at −60°C. These compounds decomposed, when heated in vacuo, to form the corresponding oxides and carbonates. They detonate violently when treated with water. Schwarz and Striebich (*38*) have shown that the reaction between liquid ammonia and chlorine monoxide takes place with explosive violence,

$$3Cl_2O + 10NH_3 \longrightarrow 6NH_4Cl + 3H_2O + 2N_2.$$

Anhydrous magnesium chloride has been prepared by suspending hydrated magnesium chloride in liquid ammonia at 20°C., and heating the resulting hexammine, $MgCl_2 \cdot 6NH_3$, to 300°C. (*39*).

The solubility of strontium nitrate in liquid ammonia over the temperature range, −65° to 43.5°C. has been determined by Portnov and Thuravlev (*40*). Some of the values found, in terms of grams $Sr(NO_3)_2$/1000 grams NH_3, are: 63.57, 381.2, 692.3, and 1321 at −65°, −3.0°, 22°, and 43.5°C., respectively. The solubility of the alkaline earth nitrates (*1, 2*) increases below 0° from barium to calcium, and from calcium to barium above 0°. According to the measurements of Smith and Koch (*41*) the approximate solubilities of the alkaline earth perchlorates are: $Ca(ClO_4)_2$, 2.2; $Sr(ClO_4)_2$, 3.0; and $Ba(ClO_4)_2$, 2.0 moles/1000 grams NH_3. Magnesium perchlorate, $Mg(ClO_4)_2$, was found to be soluble to the extent of approximately 1.7 moles/1000 grams NH_3.

A thorough investigation of the solubility of alkali chlorides in liquid ammonia over wide temperature ranges has recently been described (*42*). The solubility of potassium chloride was found to increase from 0.078% by weight at 44.2° to 0.252% at −77.2°C. The slight solubility of KCl as compared with NaCl (*1, 2*) is probably due to the fact that the former does not enter into combination with the solvent. It is of interest to point out the marked difference in the solubility behavior of these two salts in ammonia. The solubility of NaCl increases between −76.6° and −9.5°, then decreases rapidly between −9.5° and 43.0°C., while the solubility of KCl decreases regularly with increase in temperature. In the presence of ammonium chloride or sodium chloride, the solubility of KCl is almost doubled, while the effect of the presence of ammonium chloride on the solubility of NaCl depends upon the concentration of ammonium chloride. With increase in temperature, the solubility of ammonium chloride increases from 5.23% by weight at −52.9° to 54% at 8.3°C. Over this temperature range, the solid phase in equilibrium with the saturated solution is the ammonate, $NH_4Cl \cdot 3NH_3$. Studies on the systems KCl–NH_4Cl–NH_3, KCl–NaCl–NH_3, and NaCl–NH_4Cl–NH_3 gave no evidence of the formation of mixed crystals or complex salts.

Abe and co-workers have extended their studies on the solubility of sodium chloride in liquid ammonia (*1*) to include the temperature range, −30° to −60°C. (*43*). In addition to observed values over the above temperature range, they have shown that values calculated from empirical equations describing the dependence of solubility upon temperature are in good agreement with the experimental data. Calculated values for heats of vaporization (30° to −60°), heats of solution (30° to −40°), and osmotic pressure (30°), have been presented. At 25°C., the heat of vaporization was found to be 4823 cal./mol. NH_3, and the heat of solution, 6.00 kg. cal./mol. NaCl.

The solubility, electrolysis, and conductivity of sodium chloride in liquid ammonia have been studied by Vasil'ev and co-workers (*44*). Their solubility values are in agreement with those of earlier investigators (*1, 2*). They have emphasized the dependence of conductivity on solubility and have shown that conditions favorable to a maximum conductivity may be realized at the point of maximum solubility. The electrolysis of sodium chloride in liquid ammonia proceeds in accordance with the equation,

$$6NaCl + 14NH_3 \rightarrow 6NH_4Cl + 6NaNH_2 + N_2 + 3H_2.$$

Close agreement between observed and calculated values for the decomposition voltage of the saturated solution at −33° was found. The foregoing reaction has served as a basis for the development of a method for the preparation of sodium amide (*45*). The best results were obtained with temperatures below 0°, pressures of from two to three atmospheres, and a potential of four or five volts, using an iron cathode and graphite anode. Sodium amide and hydrogen are formed at the cathode, nitrogen and ammonium chloride at the anode.

The electrolysis of sodium triphenylgermanide, $(C_6H_5)_3GeNa$, in liquid ammonia solution at −33°C. has been studied by Foster and Hooper (*46*). Using a platinum anode, 10–35% yields of hexaphenyl-

digermane, $(C_6H_5)_3GeGe(C_6H_5)_3$, and approximately equivalent quantities of triphenylgermane and nitrogen were found. With a mercury anode, however, less than the predicted volume of nitrogen accompanied the formation of the above products.

The potential of the cell,

−	Na, Hg	$NaNO_3$	KNO_3	$Pb(NO_3)_2$	Pb	+
	0.09524%	0.1 *N*	satd.	0.1 *N*		

has been determined at −35°C. by Pleskov and Monoszon (*47*). E = 1.3375 v. For the cell,

−	K, Hg	KNO_3	KNO_3	$Pb(NO_3)_2$	Pb	+
	0.2216%	0.1 *N*	satd.	0.1 *N*		

they have found a value of E = 1.287 v. at −35°C. Using these results and data provided by earlier workers, they have shown that the normal potentials of sodium and potassium in liquid ammonia at −50° have the values listed in Table 3. All potentials listed are referred to the normal potential of lead as zero. The value for hydrogen and for corresponding potentials in water are included for the sake of comparison.

TABLE 3

	Pb	Na	K	H_2
E_{NH_3}	0	−2.17	−2.32	−0.34
E_{H_2O}	0	−2.58	−2.79	−0.13

It has been observed that, in contrast to all the other elements studied, the potentials of the alkali metals in liquid ammonia are more positive than in aqueous solutions. Undoubtedly, this condition, together with the relatively lower dissociation constant of liquid ammonia, offers an explanation of the remarkable stability of the alkali metals in liquid ammonia solution. Continuing their studies of electrode potentials in liquid ammonia, Pleskov and Monoszon (*48*) have determined the normal potentials of a number of other elements. Their values, referred to the normal hydrogen electrode at 20°, are listed in Table 4.

TABLE 4

Electrode	E_{NH_3}	E_{H_2O}
K/K^+	−2.73	−2.92
Na/Na^+	−2.59	−2.71
Zn/Zn^{++}	−1.27	−0.76
Cd/Cd^{++}	−0.93	−0.40
Pb/Pb^{++}	−0.42	−0.13
H_2/H^+	−0.75	0.00
Cu/Cu^{++}	−0.32	0.35
Hg/Hg^{++}	0.00	0.79
Ag/Ag^+	0.08	0.81

For sodium and potassium ions, the solvation energy has been found to be about the same in water and in ammonia. However, for the other ions studied, the energy of ammonation is greater than the energy of hydration.

Yost and co-workers (*49*) have found that, in liquid ammonia solutions of ammonium chloride at 25°, the cell, Zn(amalg., N_2), $ZnCl_2 \cdot 6NH_{3(l)}$, NH_4Cl (in $NH_{3(l)}$), f., $CdCl_2 \cdot 6NH_3$, Cd(amalg., N_1) gives reproducible and reversible E.M.F.'s. When zinc and cadmium are present as pure metals, $E_{298.2}$ = 0.3605 volt. Utilizing data provided by earlier workers, they have derived energy equations representing the stepwise deammonation of $CdCl_2 \cdot 10NH_3$. Combining these data with those of the present investigation, Yost and co-workers have calculated the free energies, heat contents, and virtual entropies of cadmium chloride and its ammonates. Similarly, they have presented provisional values for the activity coefficients of ammonium chloride in liquid ammonia solutions at 25°C. The activities of ammonium bromide and ammonium chloride in liquid ammonia at −50° have been determined by means of the hydrogen electrode (*50*). Measurements were made over the concentration range, 1.0 to 0.0001 *N*. Representative data are given in Table 5.

TABLE 5

NH_4Cl		NH_4NO_3	
C	f	C	f
0.005	0.423	0.0001	0.953
0.05	0.188	0.001	0.824
0.5	0.070	0.01	0.466
		0.1	0.216
		1.0	0.104

For the dissociation of liquid ammonia at −50°,

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-,$$

the dissociation constant was found to be $C_{NH_4^+} \cdot C_{NH_2^-} = 1.9 \times 10^{-33}$. Relative values for the activity coefficients for ammonium chloride, bromide, iodide, and nitrate, calculated from vapor-pressure data by Larsen and Hunt (*51*), show that the activities of these salts are relatively low in liquid ammonia at 25°C.

Shatenstein and Uskova (*52*) have determined the densities and vapor pressures of liquid ammonia solutions of ammonium chloride, bromide, iodide, nitrate, acetate, and sodium nitrate at 15°, and sodium chloride at 10°C. The osmotic coefficients were found to decrease in the following order:

$$NH_4I > NH_4NO_3 > NaNO_3 > NH_4Br > NaCl > NH_4Cl > NH_4C_2H_3O_2.$$

Low osmotic coefficients are believed due to the low dielectric constant of liquid ammonia, and were found to increase as the temperature was lowered.

In connection with their studies on the vapor pressures of liquid ammonia solutions of calcium nitrate and magnesium nitrate, Zeidenberg and Il'inskaya (*53*) have found definite concentrations at which the vapor pressures at room temperature do not exceed one atmosphere. For ammonium nitrate, this condition is realized at a concentration of 347 grams NH_4NO_3/100 grams NH_3 at 8°C., and for calcium nitrate, a concentration of 247.5 grams $Ca(NO_3)_2 \cdot 4H_2O$/100 grams NH_3 at 22°C. The fact that calcium nitrate does not crystallize from such solutions, when cooled to −60° or heated to 60–70°C., suggests the use of these viscous liquids as lubricants in refrigeration cycles using ammonia.

The use of the polarograph in the measurement of decomposition potentials of salts in liquid ammonia has been described by del Boca (*54*). An account has been given of the modifications of the original Heyrovsky method required for this particular work and of the factors influencing the accuracy of the results obtained. Table 6 serves to point out the marked difference between del Boca's results and those due to Groening and Cady (*55*).

TABLE 6

Salt	*Groening and Cady*	*del Boca*	*Metal Hydroxide in Water (Nernst)*
$AgNO_3$	0.80	..	0.90
$AgNO_2$	0.74	..	0.90
AgCl	0.84	..	0.90
$Cu(NO_3)_2$	0.92	1.36	1.34
$Ni(NO_3)_2$	0.94	1.89	1.91
$CdBr_2$	..	2.08	2.06
CdI_2	1.65	2.06	2.06
$Cd(NO_3)_2$	1.64	2.05	2.06
$Zn(NO_3)_2$	2.06	2.46	2.45

Del Boca's data show that, during electrolysis, the potentials required for the discharge of metal ions are identical in water and in liquid ammonia. The fact that values found for metal salts in liquid ammonia are identical with values for the corresponding hydroxides in water led del Boca to believe that this was due to the presence of water as an impurity in the liquid ammonia used. Accordingly, experiments were conducted with given salts in ammonia containing traces of water, and in strictly anhydrous ammonia. The results were identical. It should also be pointed out that Groening and Cady emphasized the importance of the elimination of water from the solvent ammonia. Since the values given for three salts of cadmium are sensibly the same, these data point to the conclusion that there is discharged at the anode a common ion having the same discharge potential as the hydroxyl ion in water, and that this is the amide ion, NH_2^-.

The absorption spectra of numerous complex ammines of cobalt, nickel, and chromium in liquid ammonia solution have been studied at low temperatures (*56*). It was found that the absorption bands are similar to those obtained with aqueous solutions. A typical example of the compounds studied is the complex, $[Co(NH_3)_5(NO_3)](ClO_4)_2$. The ultraviolet absorption spectra of liquid ammonia at its melting point (−78°), boiling point (−33.5°), and at 26°C. have been studied (*57*). Absorption has been shown to increase with temperature, with a slight shifting of the absorption bands, limits of 2320 Å., 3400 Å., and 2480 Å. corresponding to the temperatures, −78°, −33.5°, and 26°C. The liquid under 2 cm. pressure showed a continuous spectrum. A study of the near infra-red absorption spectra of liquid, gaseous, and dissolved ammonia (*58*) has shown that over the temperature range −40° to −75°C., and from 0.8μ to 1.2μ, no displacement of the bands is observed. Results of this investigation point to the existence of polymers both in the liquid and in concentrated aqueous solutions of ammonia.

Shatenstein (*59*) has extended his polarimetric studies on the ammonolysis of santonin by liquid ammonia (*2*). The investigation revealed that the reaction is markedly catalyzed by the presence of ammonium salts (acids in liquid ammonia) and is dependent upon their concentration. The catalytic activity of the ammonium salts follows the order,

$$NH_4Cl > NH_4Br > NH_4NO_3 > NH_4I > NH_4ClO_4.$$

It is to be observed that the above order is the reverse of the order in which the activity coefficients, osmotic coefficients, and conductivity coefficients for the same salts fall. The catalytic activity of various salt mixtures has also been studied. Shatenstein's initial communication (in Russian) concerning his studies on acid catalysis in liquid ammonia has been reprinted, in part, in German (*60*). This work was reviewed at an earlier date (*2*). A method by which polarimetric investigations of liquid ammonia solutions may be carried out has been described (*61*).

Jaffe (*62*) has found that a saturated solution of lithium in liquid ammonia solidifies at −180°C. and exhibits a metallic copper-like reflection. The electrical conductivity of the solid phase exhibits a temperature dependence similar to that for ordinary metals and shows a normal negative Hall effect at −190°, the value being -1.38×10^{-3} sq. cm./amp. sec. Evidence for the existence of the complex ion, $Li(NH_3)_4^+$, and for the presence of one free electron for each atom of lithium has resulted from the above studies. A study of the magnetic susceptibility of sodium in liquid ammonia solutions (*63*) has shown that, at 230°Å., sodium in a 0.5 *N* solution has an atomic susceptibility of the same order of magnitude as that of the pure metal. In a 0.017 *N* solution, the atomic susceptibility is about thirty times that of the pure metal, and in a 0.0022 *N* solution, about 100 times as great.

The X-ray diagram of cellulose in the presence of liquid ammonia has been studied by Hess and Trogus (*64*). The diagrams are influenced by the rate of evaporation of ammonia from the cellulose, and indicate the penetration of ammonia molecules into the cellulose lattice. The volumes of ammonia-hydrogen mixtures in liquid ammonia at 100°C. and at pressures of from 100 to 800 atmospheres have been measured by Wiebe and Tremearne (*65*). From these data, the partial molal volumes of both constituents were calculated. It has been suggested that the distillation of liquid ammonia might be used as a method of obtaining an increased concentration of $N^{15}H_3$ (*66*).

A rapid method for the determination of moisture in liquid ammonia has been described (*67*). A sample of ammonia is evaporated, the water absorbed by a weighed quantity of sodium hydroxide, and the ammonia dissolved in water and titrated with acid.

Patents covering processes involving the use of liquid ammonia issued during the year relate to the manufacture of ammonium sulfate (*68*) and to the prepa-

ration of sodium cyanide (*69*) and sodium nitrate (*70*). A process for the preparation of the carbamates of Na, Ca, Sr, Ba, Pb, Mg, Cu, Zn, Mn, Ni, and Ag (*71*) involves the treatment of liquid ammonia solutions of salts of these materials with carbon dioxide. Ammonium nitrate may be added to increase the solubility of the metal salts. Another patent covers the application of the above method to the preparation of potassium carbamate (*72*). The action of liquid ammonia on alkali metal bicarbonates has also been applied to the formation of the corresponding carbamates, NH_2COOM (*73*).

Unquestionably the year's outstanding contribution to the literature of liquid ammonia chemistry is E. C. Franklin's monograph, "The Nitrogen System of Compounds" (*74*). Both as a source of information and as a stimulus for future research, this work will prove to be of inestimable value. Since adequate reviews of this book have appeared elsewhere (*75*, *76*, *77*), no further comments seem necessary at this time.

Franklin and Bergstrom (*78*) have given a brief discussion of heterocyclic compounds containing nitrogen, the first of two papers being concerned with five-membered rings. They have shown how such compounds may be regarded as belonging to the nitrogen system of compounds. In their review of investigations involving the alkali metals, Alterthum and Rompe (*79*) have discussed the solubility, photochemical sensitivity, and electrical conductivity of these metals in liquid ammonia. The ammonolytic reactions of halides of elements in the fourth group of the periodic arrangement have been discussed by Schwarz (*80*) in his review of the chemistry of germanium.

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REMOVAL *of* PHOSPHATE ION

LOUIS J. CURTMAN AND THOMAS B. GREENSLADE

The City College of the College of the City of New York

The best-known methods for the removal of phosphate ion are discussed, compared, and evaluated in terms of completeness of removal of phosphate, accompanying loss of cations, time required for carrying out the procedure, ease of removal of reagent, and convenience to the student. On the basis of these comparisons certain recommendations are made.

✦ ✦ ✦ ✦ ✦ ✦ ✦

INTRODUCTION

AN EXPERIMENTAL study of the various methods for phosphate ion removal in qualitative analysis was undertaken from the standpoint of the student. His shortcomings have constantly been kept in mind, and the suggestions and recommendations herein contained are especially applicable to student work.

Of the numerous procedures proposed for the removal of phosphate ion in qualitative analysis, only three are widely used. They are: (1) the tin method, (2) the ferric chloride method, (3) the zirconium oxychloride method. Procedures using lead and bismuth salts have been proposed, but they do not seem to offer any advantages over the three mentioned above.

METHODS

The Tin Method.—Metastannic acid is formed when tin is boiled with strong nitric acid; this precipitates or adsorbs PO_4^{-3}. Since the resulting precipitate is somewhat soluble in HCl, the HCl is removed by evaporating with nitric acid.

Procedure.—Evaporate the filtrate from the copper and tin groups to about 1 ml. Add 10 ml. of concentrated HNO_3 and evaporate the solution just to dryness. Now add 20 ml. of concentrated HNO_3, 10 ml. of water, and 2 g. tin (preferably C.P., about 20 mesh). Heat the mixture to boiling and evaporate over a low flame (caution: this mixture bumps very easily!), with stirring, to about 0.5 ml. Add 20-30 ml. water, stir, allow to stand, and filter on a fluted filter.

The Ferric Chloride Method.—All the phosphates of the cations of Groups 3, 4, and 5 are soluble in acetic acid solution buffered by alkali acetate except those of the trivalent ions, Fe^{+3}, Al^{+3}, and Cr^{+3}. The precipitation of PO_4^{-3} under these conditions is complete, when an excess of these trivalent ions is present. For several reasons ferric chloride seems to be an ideal reagent for supplying this excess. It is easy to test for Fe^{+3} in the filtrate from the copper and tin groups. $FePO_4$ is the least soluble of the phosphates which may be precipitated in acetic acid solution. The solution acquires a characteristic deep brown color when an excess of Fe^{+3} has been added. Finally, the excess of Fe^{+3} may be conveniently removed by making use of the fact that $Fe(C_2H_3O_2)_3$ is extensively hydrolyzed on boiling and diluting. The excess Fe^{+3} is precipitated out as a basic salt and is removed by filtration along with the precipitated phosphates.

Procedure.—To the filtrate from the copper and tin groups, contained in a 500-ml. beaker, add NH_4OH a little at a time until a permanent precipitate forms or until the solution becomes alkaline. Add dilute HCl drop by drop with stirring until a clear solution results. Add 8 g. $NH_4C_2H_3O_2$ and 8 ml. 50% acetic acid. If the solution is red, sufficient iron is already present; if not, add $FeCl_3$ a little at a time until the solution acquires a deep brownish red color. If the color cannot be seen, because of the formation of a precipitate or the presence of colored ions, filter off a small portion of the mixture and render the filtrate alkaline with NH_4OH. If a light-colored precipitate is obtained, more $FeCl_3$ should be added to the main mixture with stirring, until a similar test gives a reddish brown precipitate

showing that Fe^{+3} is present in excess. Add sufficient hot water to make the volume about 400 ml. Heat the mixture rapidly to boiling and boil for three minutes. Filter on a large fluted filter while still hot.

The Zirconium Oxychloride Method.[1]—This method is based on the fact that $ZrOCl_2$ completely precipitates PO_4^{-3} in 0.3 *N* HCl solution. The excess Zr^{+4} is removed along with the PO_4^{-3} by precipitation with NH_4OH as $Zr(OH)_4$; the latter, after prolonged heating in the ammoniacal solution, is fairly insoluble in dilute HCl.

Procedure.—To the filtrate from the copper and tin groups add 2 g. of NH_4Cl and 10 ml. $ZrOCl_2$ solution (50 mg. Zr^{+4} per ml.) drop by drop, stirring vigorously. Add 0.2 g. of asbestos or one Fisher filtration accelerator. Render alkaline with NH_4OH and boil for 2 minutes. Neutralize with dilute HCl, add 10 ml. 3 *N* HCl in excess, and boil for 3 minutes. Filter hot on a fluted filter.

EXPERIMENTAL

Nearly 100 test analyses were made, using known solutions containing cations in amounts ranging from 5 to 100 mg., and PO_4^{-3} in amounts up to 500 mg. In these experiments Ni, Fe, Ba, and Mg were used to determine the loss of metal ions, since these cations are convenient to determine and were thought to be representative. Barium was roughly determined by precipitating it as the chromate and comparing the size of the precipitate with that obtained in a standard solution. The estimations were greatly facilitated by the use of a specially devised precipitation tube to be described in a forthcoming article by Curtman and Adler. In addition to the three methods described above, the variation in the ferric chloride method outlined by Noyes[2] was also tried. Since the results closely agreed with those given by the above method, they are both included under one heading. Several runs were made by a student using all three methods. This was done in order to observe the time required to complete each procedure as well as the ease with which the student was able to perform the operations.

RESULTS

The results of this investigation are summarized in the accompanying chart. The small letters refer to the notes which immediately follow the chart.

COMMENTS AND CONCLUSIONS

As the results show, all three of the methods considered are quite efficient in so far as the removal of phosphate ion is concerned. Therefore, an evaluation of the procedures must be based upon the other factors involved. In both the tin and the $FeCl_3$ methods, the loss of cations is very serious. Although this might not necessarily cause the student to miss metals, it would prevent a correct estimation of the quantities of the cations present. A consideration of the time involved in carrying out the procedures favors the $ZrOCl_2$ method. Students find the $FeCl_3$ procedure quite inconvenient since it involves boiling a large volume of solution and filtering the latter while hot. The resulting filtrate is altogether too large to be used in the analysis for the remaining metals, so that a tedious evaporation to a smaller volume is imperative. The appearance of Zr in Group 3 does not cause sufficient trouble to make this a serious drawback to the $ZrOCl_2$ procedure. The results of this investigation clearly show that from the standpoint of efficiency, rapidity of execution, and convenience, the $ZrOCl_2$ method is the best procedure for the removal of phosphate ion in qualitative analysis.

COMPARATIVE STUDY OF METHODS FOR REMOVAL OF PHOSPHATE ION

	Removal of PO_4^{-3}	Loss of			Time Required (*b*)	Ease of Removal of Excess Reagent	Convenience to Student
		Ni	Fe	Ba (*a*)			
Tin Method	Complete only when a large amount of tin is used (*c*)	Practically no loss	Almost complete loss	Loss increases greatly as the concentration of Ba^{++} increases	40 minutes	Completely removed as metastannic acid (*d*)	Involves a number of tedious evaporations (*e*)
$FeCl_3$ Method	Complete	Some loss in the higher concentrations		Very great loss (*f*)	45 minutes	Removed as basic salt (*g*)	The large volume makes handling rather difficult
$ZrOCl_2$ Method	Complete	Practically no loss	Small constant loss (*h*)	Practically no loss	30 minutes	Comes down with Fe and Mn in Group 3 (*i*)	Removal of excess reagent somewhat inconvenient

(*a*) Tests were also made to determine how much Mg was lost in these procedures. The results so closely approximated those obtained for Ba that it was decided not to include them in the chart.
(*b*) Time required by a student to complete procedure.
(*c*) Experiment showed that if much more than 2 g. of tin was used, the metallic ions were almost completely lost in the cases of Fe and Ba.
(*d*) No test for tin was obtained in the filtrate after the metastannic acid had been filtered off. There were no traces of impurities of Cu or Pb in the tin used.
(*e*) This mixture of strong nitric acid and metastannic acid has a marked tendency to bump when heated. The element of danger involved should not be ignored.
(*f*) As much as 40 mg. was lost from a solution originally containing 50 mg. of Ba.
(*g*) Some of the Fe came through colloidally.
(*h*) No test for Fe was obtained after phosphate removal when the original solution contained 5 mg. of Fe. However, a solution containing 50 mg. of Fe was found to have lost only about 5 mg. of Fe during the treatment with $ZrOCl_2$.
(*i*) A great deal of the excess Zr will be precipitated along with the PO_4^{-3}, but some redissolves when the solution is made acid and therefore must be considered in Group 3.

[1] CURTMAN, MARLIES, AND PLECHNER, *Chem. News*, **129**, 299 (1924).

[2] NOYES, "Qualitative chemical analysis," The Macmillan Co., **1922**, p. 105.

APPARATUS *for* MAKING SPECTRAL FLAMES *of the* ALKALI *and* ALKALINE EARTH METALS

J. F. BIRMINGHAM, JR., AND W. H. WOOD

Chandler Laboratories, Columbia University, New York City

IT IS often necessary to produce colors characteristic of Li, Na, K, Ca, Ba, and Sr compounds for classroom and laboratory purposes. The difficulty usually encountered is that the colors do not last, and they require constant attention when used for periods of one hour or more.

The simplest method of production is to form a bead of some salt of the metal upon a platinum wire, and hold it in the non-luminous flame of a burner. The bead must consist of some material that melts easily, and yet does not vaporize too rapidly at the temperature of a Meker flame. The chlorides of calcium, barium, and strontium melt easily and hydrolyze to highly refractive oxides at higher temperatures. The beads of these salts produce brilliantly colored flames. On the other hand, the salts of lithium, sodium, and potassium are quite volatile, and except for sodium salts, minute traces of which give good colors, the beads give flames that are brilliant, but do not last more than several minutes.

Flames larger and more intense than those obtainable from salt beads may be produced by means of the atomizer outfit described below. It is very simple to construct and, once set in operation, requires no further attention for several hours.

The apparatus consists of a 250-cc. Erlenmeyer flask (Figure 1), fitted with a two-hole rubber stopper. This holds the nozzle, which is made of ordinary 6-mm. glass tubing bent at right angles 6 to 8 cm. from one end, and bent and drawn out to a tip at the other. It is made so that the latter bend rests on the bottom of the flask, with the tip 1 to 2 cm. from the side of the flask and perpendicular to it. Since the wall of an ordinary pyrex Erlenmeyer makes an angle of 70° with the base, the bend near the tip should be approximately 70° from the vertical. This is made clearer by the diagram. The inside diameter of the tip should not be much more than 1 mm.

With 100 cc. of salt solution—2 molar—in the flask, and with an air supply connected to the nozzle, a rapid stream of fine bubbles issues from the tip and is further subdivided by striking the side of the flask. Consequently, a very fine spray is produced which is entrained in the current of air and passes out of the flask through a straight glass tube, *T*, and the air vent, *V*, of a burner, causing the spectral flame characteristic of the metal whose salt solution is contained in the flask.

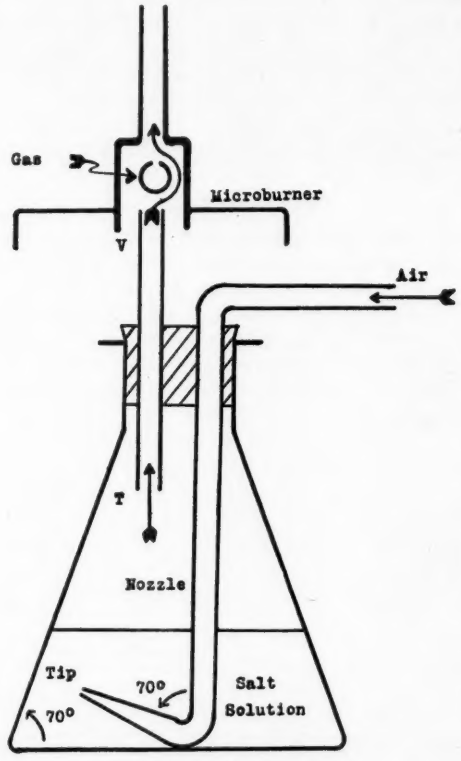


FIGURE 1.—ATOMIZER OUTFIT

The burner is a standard microburner which was chosen because the air vent was in the base, making it a simple matter to introduce the salt spray. The flame is non-adjustable, non-luminous, 10 to 14 cm. high, and the air stream from a 1-mm. nozzle cannot blow it out. This burner has the added advantage of being small and light, and when mounted above the flask, renders the whole atomizer unit compact.

A battery of six such units has been in use for general chemistry courses at this university for the last four semesters. Figure 2 is a photograph of this outfit. The air inlet tubes are connected to other tubes which pass through the back-board and are held by small rubber stoppers; the outlet tubes of two atomizers are connected to an inverted Y-tube, the upper end of which is placed inside the air vent of a microburner. Thus

only three burners are required, all fed from the same gas line by a glass tube with three outlets. The air supply is connected with any one of the flasks and the color will be maintained as long as required.

The spectral lines of the metals may be conveniently viewed by means of a small pocket spectroscope. This instrument has the advantage of permitting one to see all the lines, from violet to red, at once.

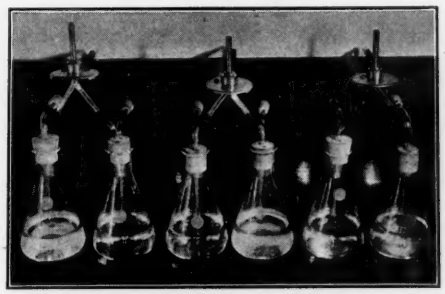


FIGURE 2.—BATTERY OF SIX ATOMIZER UNITS SALTS OF Na, K, Li, Ca, Ba, Sr

When the class is large and it is desired to show each member individually the spectral lines, some device for making rapid changes from one solution to another is of value. A six-way valve in the air line may be added to the apparatus, but it is expensive. At the suggestion of Mr. J. O. Percival, the adaptor shown in Figure 3 has been used in our outfit. A one-inch brass rod was drilled through the center and turned on a lathe so that a No. 2 rubber stopper fitted closely inside. This adaptor was connected to the air supply and No. 2 stoppers were put on the ends of the air inlet tubes in the back. Rapid changes may now be made merely by shifting the adaptor from one inlet to another.

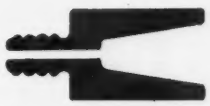


FIGURE 3.—ADAPTOR FOR NO. 2 RUBBER STOPPER

CORRESPONDENCE

REFERENCE NEEDS OF THE CHEMIST IN INDUSTRY

To the Editor

DEAR SIR:

The editorial in your November, 1935, issue, concerning the quality of chemical graduates, was very interesting to me, because of my interests for a number of years in editing and compiling of data for the Hodgman-Lange Handbook of Chemistry and Physics and more recently my own Handbook of Chemistry. Perhaps I am somewhat biased in my point of view, but to use your own words, "we probably stress the side of the picture that we know best."

So few of the teachers of chemistry appreciate the difficulty which many of their students encounter after they leave the university. Their employers are often men with a business or legal training who have no conception of the difficulties of a technical man with limited library facilities. This difficulty is noticed especially by the recent graduate who locates with a small organization, which is often located in a small city. The employer does not provide much of a library and does not realize that a technical man cannot possibly remember all the data he may have occasion to use. The chemist for a small company is often the only technical man in the organization and frequently is called upon for advice in fields other than his own specialty. Is it any wonder that many such employers criticize technical training when their employee displays ignorance? But in many cases this ignorance is not because of a poor university training but because there is available to the employee only a limited amount of data furnished by his former textbooks—books which were designed to teach principles and not to substitute for encyclopedias.

Many teachers of chemistry show little concern for this difficulty, which so many of their students encounter after graduation; this, I suppose, is due to the fact that most teachers have always had available a good college or university library. I hope the time will come when more of our teachers will see to it that their chemistry students enter their professional careers possessed of at least a few books of general reference.

N. A. LANGE

SANDUSKY, OHIO

N. Y. S. S. T. A. RESOLUTION

To the Editor

DEAR SIR:

At the recent meeting of the New York State Science Teachers Association at Syracuse, N. Y., the following resolution (No. 5) was adopted:

Resolved: That it is the sense of this association that we would be glad to support one National Organization of Science Teachers, and that we regret that there is an apparent duplication of effort in this direction. That one important function of such a National Organization should be the development of a single National Publication devoted to the teaching problems in the science sequence from grades one to twelve, utilizing the foundation already laid by the science teaching journals now in existence. That copies of this resolution be sent to the department of science instruction of the National Education Association, to the American Science Teachers' Association, to *School Science and Mathematics*, to *Science Education*, and to the JOURNAL OF CHEMICAL EDUCATION.

LOUIS J. MITCHELL, *Sec.-Treas.*

DANSVILLE CENTRAL HIGH SCHOOL
DANSVILLE, N. Y.

SIMPLE COLORIMETRIC ANALYSIS *for* LABORATORY INSTRUCTION

LANDON A. SARVER

University of Minnesota, Minneapolis, Minnesota

CONSIDERING the great importance and numerous advantages of photometric methods of quantitative chemical analysis, it is a great pity that comparatively few chemists receive any instruction whatever along this line in their regular college courses. The reason for this undoubtedly lies in the fact that colorimeters are thought to be too delicate and costly for use by large groups of inexperienced students, while even the matched Eggertz tubes required for the dilution method would represent a considerable outlay of money for a single special experiment.

The author has used for several years a standard series method for the determination of ammonia, which is sufficiently accurate for instructional purposes, but which requires only ordinary rectangular medicine bottles for making the color comparisons. Inequalities in the dimensions of the bottles are not great enough to affect the results seriously, and about twelve hundred students have performed the experiment with a remarkable degree of success.

Principle of the Method. When a solution containing a small amount of an ammonium salt is treated with an alkaline solution of potassium mercuric iodide (Nessler's solution), a yellow color is produced, the intensity of which is dependent upon the concentration of ammonium ion; if this be compared with equal thicknesses of a series of standards, the quantity of ammonia present may be easily estimated.

Nessler's Solution. The concentrated stock solution is prepared by dissolving 150 g. of potassium iodide in 100 ml. of distilled water, adding 110 g. of iodine, and then 140–150 g. of free mercury. The flask is shaken continuously and vigorously for 10–15 minutes, or until nearly all of the dissolved iodine has disappeared, during which time the solution becomes quite hot; when the reddish iodine solution has begun to become visibly pale, though still red, it is cooled in running water and the shaking continued until the red has been replaced by the greenish color of the double iodide, after which the solution is decanted off from the surplus mercury; the latter is washed with liberal quantities of distilled water, and the solution diluted to two liters.

The finished reagent is made as needed by diluting 150 ml. of the stock solution to one liter with 5% sodium hydroxide solution; this reagent is made less alkaline than the conventional one in order to permit the comparison of higher concentrations of ammonium salts, without the formation of a precipitate.

Standard Ammonium Chloride Solution. About 0.0628 g. of pure dry ammonium chloride is weighed as accurately as possible, and diluted to one liter in a volumetric flask; if exactly this amount be taken, the concentration will be 0.02 mg. of NH_3 per milliliter.

Samples. A suitable stock solution is obtained by dissolving 6.28 g. of pure dry ammonium chloride, and making up to exactly ten liters with distilled water. Individual samples are dispensed in medicine bottles by measuring out 8.0 to 20.0 ml. of this solution, in steps of 0.5 ml., and adding some water at random.

Water. In most cases, distilled water freshly drawn from the regular laboratory supply will be found sufficiently pure; if desired, it can be redistilled, discarding the first and last portions.

Procedure. All apparatus must be washed with fresh distilled water. The unknown sample is transferred quantitatively to a 250 ml. volumetric flask, diluted to the mark, and mixed well. One buret is filled with distilled water, the other with standard ammonium chloride, after rinsing with several portions of the solution. Rectangular medicine bottles of suitable size should be labeled on their bottoms X, and 1 to 9, respectively.

An approximate determination is first made by measuring 5, 10, 15, 20, and 25 ml. of the standard ammonium chloride, and one 25-ml. pipetful of the unknown sample solution, into a series of bottles, diluting to exactly 45 ml. with distilled water in each case, mixing by gentle rotation, adding 5 ml. of the Nessler's reagent to each, mixing again, and comparing against a blue sky or other uniformly illuminated background. The approximate concentration of the unknown may thus be easily determined.

For the final comparison, another unknown and nine standards of suitable concentration varying by steps of 0.5 ml. of the ammonium chloride solution, are prepared and compared in the same way. The decision is much more difficult this time, but it is rare for a person of average color perception to be in error by more than one 0.5 ml. step.

The number of milligrams of NH_3 in the sample may be calculated by multiplying the number of milliliters of ammonium chloride solution in the matching standard by ten times its concentration.

Summary. A colorimetric analysis problem which is suitable for laboratory instruction and which illustrates an important conventional method, but which requires no delicate or expensive apparatus, has been given.

MATHEMATICAL PROBLEM PAGE

Directed by EDWARD L. HAENISCH

Montana State College, Bozeman, Montana

PROBLEMS

1. Show that the solution of $dy/dx = Ky$ can be written in the form of a geometrical progression, $y = y_0C^x$, where y_0 is the value of y when $x = 0$. Evaluate C in terms of y_0 and a known value of x and y.

2. Use the data of Taylor and Close [*J. Am. Chem. Soc.*, **39**, 422 (1917)] to show that the conversion of hydroxyvaleric acid into valeracetone is a first-order reaction. The reaction is followed by titrating a definite volume of solution with standard alkali. Hydrogen ion is present as a catalyst. The volume of the alkali required when the reaction is complete represents the amount of base needed to titrate the catalyst and must be subtracted from the total volume of alkali used at any time to obtain the volume of alkali required to titrate the hydroxyvaleric acid present. Use the following methods. (1) Show that the data satisfy a first-order equation, $dc/dt = kc$. (2) Show that the data satisfy the geometric progression form of Problem 1. (3) Use a graphical method. (Hint: What does the differential equation state about the slope of a plot of log c *vs.* t?)

Time in Minutes	*Volume of Alkali Required*	*Time in Minutes*	*Volume of Alkali Required*
0	19.04	204	14.41
48	17.60	238	13.94
76	16.90	289	13.37
124	15.80	Complete	10.71

3. A 3-liter bulb with two side openings is filled with air which contains 21% oxygen by volume. Oxygen flows into the bulb through one of the side openings at the rate of 200 cm.^{3} per minute and an equal volume of gas in the bulb escapes through the other opening. Assume that mixing of the gases in the bulb is instantaneous and complete. How long a time will be required for the oxygen content of the bulb to reach 80% by volume?

REFERENCE

HITCHCOCK AND ROBINSON, "Differential equations in applied chemistry," John Wiley & Sons, Inc., New York City, **1923.**

SOLUTIONS TO APRIL PROBLEMS

1. (*a*) $xdy + (x + y)dx = 0$

$dy/dx + y/x = -1$

$e^{\int P dx} = e^{\int \frac{dx}{x}} = e^{\ln x} = x$

Using the formula:

$$y = \frac{1}{x}\left[\int -x dx + C\right] = \frac{1}{x}\left[-\tfrac{1}{2}x^2 + C\right] \text{ or } 2xy + x^2 = C$$

(*b*) $\dfrac{dy}{dx} + \dfrac{Ky}{a - x} = \dfrac{Kx}{a - x}$

$$e^{\int P dx} = e^{K\int \frac{dx}{a-x}} = e^{-K\ln(a-x)} = e^{-\ln(a-x)^K} = \frac{1}{(a-x)^K}$$

$$y = (a - x)^K\left[\int \frac{Kx\,dx}{(a-x)^{K+1}} + C\right]$$

Integration by parts must be used to evaluate $\int \dfrac{Kx\,dx}{(a-x)^{K+1}}$

$\int u dv = uv - \int v du$. Let $v = (a - x)^{-K}$, $dv = -K(a - x)^{-(K+1)}(-dx) = Kdx/(a - x)^{(K+1)}$

$u = x$ and $du = dx$

$$\int \frac{Kx\,dx}{(a-x)^{K+1}} = \frac{x}{(a-x)^K} - \int \frac{dx}{(a-x)^K} = \frac{x}{(a-x)^K} - \frac{1}{K-1}(a-x)^{1-K}$$

$$y = C(a - x)^K + x - \frac{a - x}{K - 1}$$

(*c*) $\dfrac{dy}{dx} + \dfrac{y}{\cos^2 x} = \dfrac{\tan x}{\cos^2 x}$

$dy/dx + (\sec^2 x)y = \tan x \sec^2 x$

$y = e^{-\int \sec^2 x dx}\left[\int e^{-\int \sec^2 x dx} \tan x \sec^2 x\, dx + C\right]$

$\int \sec^2 x\, dx = \tan x$; $\int e^{\tan x} \tan x \sec^2 x dx$ is of the form $\int e^u . u\, du$. Using formula No. 402 in Peirce's Tables $\left[\int xe^{ax}dx = \dfrac{e^{ax}}{a^2}(ax - 1)\right]$

we obtain $\int e^{\tan x} \tan x \sec^2 x\, dx = e^{\tan x}(\tan x - 1)$

$y = (\tan x - 1) + Ce^{-\tan x}$

(*d*) $\dfrac{dy}{dx} + \dfrac{2}{x}y = 3x^2y^{4/3}$

Multiply by $-(1/3)y^{-4/3}$

$-(1/3)y^{-4/3}\dfrac{dy}{dx} - \dfrac{2}{3x}y^{-1/3} = -x^2$

This equation is linear in $y^{-1/3}$. Let $u = y^{-1/3}$;

$\dfrac{du}{dx} = -(1/3)y^{-4/3}\dfrac{dy}{dx}$

$\dfrac{du}{dx} - \dfrac{2u}{3x} = -x^2$

$e^{\int P dx} = e^{-2/3\int \frac{dx}{x}} = e^{-(2/3)\ln x} = e^{-\ln x^{2/3}} = 1/x^{2/3}$

$$u = x^{2/3}\left[\int -\frac{x^2}{x^{2/3}}dx + C\right] = x^{2/3}[-(3/7)x^{7/3} + C]$$

$$= \frac{3}{7}x^3 + Cx^{2/3}$$

$7y^{-1/3} = C'x^{2/3} - 3x^3$

2. $dx/(a - x) = K_1dt$; $\ln(a - x) = K_1t + C$

When $t = 0$, $x = 0$, and $C = \ln a$

$$\ln\frac{a - x}{a} = K_1t;\ a - x = ae^{-K_1t};\ x = a(1 - e^{-K_1t})$$

Substitution of this value of x in the equation for dy/dt produces an equation linear in y and its derivatives.

$dy/dt = K_2[a(1 - e^{-K_1t}) - y]$

$dy/dt + K_2y = aK_2(1 - e^{-K_1t})$

$e^{\int P dt} = e^{\int K_2 dt} = e^{K_2t}$

Using the formula:

$y = e^{-K_2t}[aK_2(\int e^{K_2t}dt - \int e^{(K_2-K_1)t}dt) + C]$

$y = e^{-K_2t}\left[ae^{K_2t} - \dfrac{aK_2}{K_2 - K_1}e^{(K_2-K_1)t} + C\right]$

When $t = 0$, $y = 0$,

$0 = a - \dfrac{aK_2}{K_2 - K_1} + C$ or $C = \dfrac{aK_1}{K_2 - K_1}$

$y = a - \dfrac{aK_2}{K_2 - K_1}e^{-K_1t} + \dfrac{aK_1}{K_2 - K_1}e^{-K_2t}$

3. Let N and λ_1 refer to Io and M and λ_2 refer to Ra.

$dN/dt = -\lambda_1 N$ (1)

The amount of Ra is equal to the amount supplied by the decomposition of Io less the number of Ra which has changed into Rn.

$dM/dt = \lambda_1 N - \lambda_2 M$ (2)

The solution of (1) is $\ln N = -\lambda_1 t + C$.

When $t = 0$, $C = \ln N_0$ where N_0 is the number of Io particles originally present.

$\ln N/N_0 = -\lambda_1 t$ or $N = N_0 e^{-\lambda_1 t}$ (3)

Substituting this value in (2)

$dM/dt = \lambda_1 N_0 e^{-\lambda_1 t} - \lambda_2 M$

$dM/dt + \lambda_2 M = \lambda_1 N_0 e^{-\lambda_1 t}$

This is a linear equation in M whose solution is

$$Me^{\lambda_2 t} = \int \lambda_1 N_0 e^{(\lambda_2 - \lambda_1)t}\, dt + C = \frac{\lambda_1 N_0}{\lambda_2 - \lambda_1} e^{(\lambda_2 - \lambda_1)t} + C$$

When $t = 0$, $M = 0$, and $C = -\dfrac{\lambda_1 N_0}{\lambda_2 - \lambda_1}$

$$M = \frac{\lambda_1 N_0}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

It is necessary to compute λ_1 and λ_2. For Io, by the use of (3) and the half life given:

$$\ln 0.5 = -\lambda_1 \times 7.6 \times 10^4 \times 365 \times 24 \times 3600^*$$

$$\text{or } -\lambda_1 = \frac{2.303 \log 0.5}{7.6 \times 10^4 \times 365 \times 24 \times 3600} = \frac{-2.303 \log 2}{7.6 \times 10^4 \times 365 \times 24 \times 3600}$$

and $\lambda_1 = 2.9 \times 10^{-13}$ sec.$^{-1}$

For Ra, $\lambda_2 = 1.373 \times 10^{-11}$ sec.$^{-1}$

10,000 yrs. $= 3.15 \times 10^7$ sec. yr.$^{-1} \times 10^4$ yr. $= 3.15 \times 10^{11}$ sec.

The amount, N, of Io remaining, expressed in mols. present, is

$$\ln(N/1) = -\lambda_1 t = 2.9 \times 10^{-13} \times 3.2 \times 10^{11}$$

$$\log N = \frac{-2.9 \times 3.2 \times 10^{-2}}{2.3} = -0.038 = -1 + 0.962 = 9.962 - 10$$

$N = 0.92$ mol.

The amount, M, of Ra present is:

$$M = \frac{2.9 \times 10^{-13} \times 1}{1.373 \times 10^{-11} - 0.0029 \times 10^{-11}} (e^{-2.9 \times 10^{-13} \times 3.2 \times 10^{11}} - e^{-1.4 \times 10^{-13} \times 3.2 \times 10^{11}})$$

$$= 2.1 \times 10^{-2} (e^{-0.09} - e^{-4.5})$$

Using a table to evaluate the exponentials

$M = 2.1 \times 10^{-2} (0.914 - 0.011) = 0.018$ mol.

4. $di/dt + Ri/L = E/L$

$e^{\int P dt} = e^{\int R dt/L} = e^{Rt/L}$

$i = e^{-Rt/L}[\int (E/L) e^{Rt/L}\, dt + C]$

$= e^{-Rt/L}[(E/R) e^{Rt/L} + C]$

$= Ce^{-Rt/L} + E/R.$

If when $t = 0$, $i = 0$

$$i = \frac{E}{R} - \frac{E}{R} e^{-Rt/L}$$

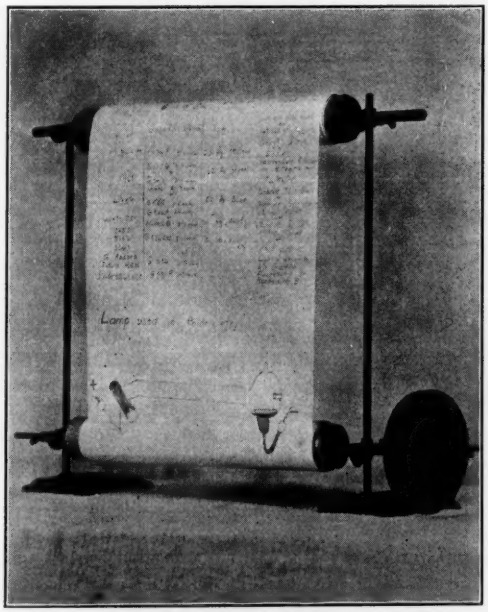
* It is customary to express γ in sec.$^{-1}$; therefore the conversion of years to seconds.

METHOD OF ILLUSTRATING LECTURES TO SMALL GROUPS

GEORGE W. ECKERT

University of Missouri School of Mines and Metallurgy, Rolla, Missouri

WHERE projection machines or sufficient board space are not available for a large number of illustrations, the apparatus shown in the photograph affords an inexpensive method of presenting drawings and tables to a small audience. This method has been employed with success by using a soft pencil on plain white wrapping paper. One-hole rubber stoppers serve to fit into the ends of the cardboard rolls to which the ends of the paper are pasted. The advantages are that the drawings or tables can be rolled back with ease, and time is saved by having the illustrations ready beforehand and in such a manner that they are fully explained.



APPARATUS FOR ILLUSTRATING LECTURES

PHILLIPS MEDAL AWARDS

The eighteenth and nineteenth Francis C. Phillips medals in chemistry were awarded in the University of Pittsburgh at the Scholars Day exercises on March 13th. This medal is awarded annually to the candidate for the B.S. degree in chemistry who has the finest record during his undergraduate residence. Messrs. John J. Griffith and George W. Gerhardt, both members of Pittsburgh families, rated so closely that a medal was awarded to each.

A. T. Burtsell
F. B. Dains
Tenney L. Davis
Spurgeon Gage
J. Howard Graham
B. Clifford Hendricks

ABSTRACTS

R. A. Baker, *Abstract Editor*

J. W. Howard
D. C. Lichtenwalner

Greta Oppe
C. M. Pruitt
Leopold Scheflan
E. D. Walter
Sidney Weinhouse
G. H. Woollett

KEEPING UP WITH CHEMISTRY

Waxing important. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **109**, 1–2 (Feb., 1936).—Since earliest times man has devised all sorts of uses for wax. It has been used for putty, for making cold cream, and for polishing wood. Much of it is used in church candles. Tallow and stearic acid are also used for candles. These are fatty substances rather than waxes, but they burn similarly. Paraffin, a hydrocarbon derived from petroleum, and ceresin, a refined mineral product, are also useful as wax substitutes. Candelilla, a fairly cheap and plentiful vegetable wax, has wax-like properties. Sperm oil is chemically a wax. Then there is Japan wax used in water-proofing mixtures, also bayberry wax, and shellac wax.

The most important wax in point of industrial utility is carnauba wax, the yellow dust that forms on the leaves of a particular palm tree in Brazil, but only when the tree grows under desert conditions: a sort of adaptation to help the tree to withstand low humidity. The natives scrape the wax off, then boil the leaves to remove part of the residue. The demand for this wax is increasing faster than the supply and various measures are necessary to protect the industry. The finest polishes for wood and leather are mixtures of carnauba wax, either emulsified in water mixtures with the aid of soap, or in turpentine solution along with paraffin, ceresin, and other modifiers.

Vegetable substitutes for carnauba are not forthcoming. Only sugar-cane wax and raphia wax are remotely like carnauba. Attention is now focused upon synthetic waxes, or more correctly, semi-synthetic waxes, based principally on "montan" wax, a fossil residue of the waxes of former plants found in peat, brown coal, shales, lignite, and other plant remains. One American manufacturer recently produced a whole line of montan waxes at reasonable prices, with melting points from that of beeswax to that of carnauba wax (184°F.). These newer products should not be expected to replace the waxes, but with proper experimentation they may be found to achieve the same result or produce results not possible before. G. O.

Light material. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **109**, 3 (Feb., 1936).—The new "I. E. S." type of lamp is calling our attention to better illumination. Holland has brought out a super high-pressure mercury-vapor discharge lamp with a tungsten wire electrode sealed into each end of a quartz bulb, with an interposed layer of glass to compensate for the difference in expansion between tungsten and quartz. Another newcomer in America will be a capillary tube mercury-vapor lamp which is small enough to rest in the palm of the hand. Within is a single drop of mercury which vaporizes when the lamp is turned on. Dyes of the coal-tar derivatives, such as rhodamine, may be used on the shades to supply the red rays which are lacking. In Germany they are experimenting with new lamp-shade paper made to resemble parchment. In the glow-lamp field, there is new application of the neon tube. The lamp is a bulb much like that of an ordinary electric light instead of an elongated tube. The luminous glow is controlled over the cold electrodes within by means of an oxide film, so that letters or even pictures are caused to appear. G. O.

The purification of water for drinking. A. H. Waddington. *Chemistry & Industry*, **55**, 65–7 (Jan. 24, 1936).—The first successful, large-scale, water purification plant was constructed in England in 1829. It was a slow sand filter. Chemicals were first used in conjunction with filtration in the United States in 1890. Since different supplies of water require different chemical treatment it is not possible to give here more than a general outline of the modern processes. If water is taken from a river it is often advantageous to provide for some settling previous to the initial chemical treatment. Aluminum sulfate is the usual coagulant, while pH is usually increased with chalk, lime, or sodium aluminate. The mixture is vigorously agitated and then time is allowed for settling and filtration. The water for the filter is clear and colorless, but usually of too low a pH for most purposes. It may also need to be sterilized. The pH is raised with sodium carbonate or lime water, and sterilization is accomplished with chlorine, chloramine (from reaction between ammonia and chlorine) or ozone. E. R. W.

Some trends in the petroleum industry. B. T. Brooks. *The Chemist*, **12**, 333–6 (Nov., 1935).—We may expect a marked increase in necessary imports of petroleum and in the prices of petroleum products within five to eight years due to a depletion of our own supplies. The fear of a shortage of petroleum which was prevalent about ten years ago has largely been dissipated through discoveries of new high-producing oil fields and through the development of deep drilling. It is doubtful if new discoveries or new developments in this country will again postpone the time of a serious depletion of our crude-oil supplies. Petroleum substitutes will become very important; among these will be found oil from oil shale, oil produced by hydrogenation of coal, oil made by reduction of water gas. E. R. W.

Some sewage disposal methods. W. D. Turner. *The Chemist*, **12**, 337–42 (Nov., 1935).—Sewage from cities may be disposed of by dilution, by screening and dilution, by chlorination and screening, or by more modern methods which are usually much more effective and desirable than those named. These modern methods are: (1) septic treatment, (2) chemical precipitation, and (3) biochemical reduction. The biochemical reduction is the newest and in many cases the best of these methods. It is particularly to be preferred when the disposal has to be accomplished in a thickly settled region where odor control and sludge removal are important and where space is at a premium. E. R. W.

Feeding experiments with mixtures of highly purified amino acids. VIII. Isolation and identification of a new essential amino acid. R. H. McCoy, C. E. Meyer, and W. C. Rose. *J. Biol. Chem.*, **112**, 283–302 (Dec., 1935).—A hitherto unknown growth essential has been isolated in pure, crystalline form, and identified as one of the four optically active α-amino-β-hydroxy-η-butyric acids. Several of its derivatives have been prepared and described.

With an otherwise adequate diet, approximately 0.6% of α-amino-β-hydroxybutyric acid is the minimum amount necessary to induce maximum growth in white rats. The feeding trials described constitute the first successful attempt to rear animals on a ration containing purified amino acids as the sole source of nitrogen. E. D. W.

The application of X-ray methods to chemical problems. R. Brill and F. Halle. *Angew. Chem.*, **48**, 785–95 (Dec. 21, 1935).—X-ray diagrams can be used for the identification of substances. They allow the determination of the presence of mixtures, mixed crystals, compounds, and allotropic and polymorphous modifications. X-ray studies at various time intervals make possible the study of reactions which alter the crystal lattice, particularly the topochemical reactions and diffusion in solids. The various constituents of mixtures can be determined according to the Debye-Scherrer method. The size and shape of submicroscopic crystals can be found, as well as disturbances of the crystal lattice. The arrangement and orientation of crystallites can be determined as well as the distances in atomic and molecular structures. By X-ray diagrams it is also possible to determine the symmetry and configuration of molecules, molecular weight, density, and the arrangement of the atom in crystals. A large number of illustrations is given. L. S.

Delinting cotton seed. A new market for concentrated sulfuric acid. W. J. Murphy. *Chem. Industries*, **38**, 128–9 (Feb., 1936).—Possible additional consumption of thirty thousand tons of crude sulfur annually is indicated in a large-scale commercial method for delinting cotton seed. In terms of concentrated acid,

the process opens up a new market of over one hundred thousand tons in the South and Southwest.

The first suggestion of decorticating seed with concentrated acid appeared in two British patents, granted in 1874-1875, so that the idea is definitely a very old one.

The first unit has now been in operation sufficiently long to demonstrate the efficiency of the process and disclose where improvements can be introduced. These are of a mechanical nature, having to do with a more efficient arrangement of the equipment and the more even flow of the seed through the process.

The practice of removing lint from cotton seed before planting has much to recommend it. In the first place, closer inspection and selection are thereby made possible. Furthermore, the fibrous layer affords an excellent shelter for bacteria and spores which later carry disease to the growing cotton plants.

Appreciating the value of the process as an additional source of consumption of sulfur and sulfuric acid, the technical department of Freeport Sulphur Company has coöperated with the workers of the Arizona State Experimental Station and is lending every assistance possible to the future commercial introduction of the process in other important cotton-growing sections.

A. T. B.

Solid CO_2 as a rat killer. ANON. *Chem. Industries*, **38,** 170 (Feb., 1936).—According to the *Chemiker-Zeitung*, solid carbon dioxide has been successfully used for some time past in the destruction of rats. The method employed is to place pieces of solid carbon dioxide about the size of a hazel nut in each of the rat holes, and to stop up the holes with broken glass and earth or gypsum. Application is best effected in the morning. It is stated that the rats are suffocated by the odorless gas without awakening. A. T. B.

Organic substances hold promise as insecticides. ANON. *Chem. Industries*, **38,** 170 (Feb., 1936).—Organic substances now seem to hold more promise as insecticides for the future than do inorganic, according to Lee A. Strong. Dept. of Agriculture chemists are directing most of their research in this field to compounds that are either extracted from plants or synthesized from products derived from natural gas, petroleum, shale oil, coal, or plant materials. In his latest report for the Bureau of Entomology and Plant Quarantine, Mr. Strong, Chief of the Bureau, discusses several promising organic insecticides. A. T. B.

Scientific furniture polish formulation. C. F. MASON. *Chem. Industries*, **38,** 173 (Feb., 1936).—From this discussion it would appear that no combination of materials could even approximate the ideal for a furniture polish which is to be used indiscriminately by the public upon furniture and interior wood work. Such is indeed the case. However, three formulas for polishes which will not harm lacquer, oil varnish, and spirit varnish coatings and will damage water paints, some spirit varnishes, and stains only after long contact, are given; the criterion being close observation of the rubbing cloth.

1.	
Cider vinegar	17 lb.
Petroleum Vmp.	31 lb.
Turpentine	19 lb.
Alcohol Denat.	3 lb.
Linseed oil (b)	14 lb.
Linseed oil (r)	16 lb.

2.	
Cider vinegar	17 lb.
Petroleum Vmp.	31 lb.
Turpentine	19 lb.
Linseed oil (b)	33 lb.
Lanette wax	10 lb.
Water	90 lb.

3.	
Paraffin oil	11 lb.
Petroleum Vmp.	22 lb.
Linseed oil (r)	11 lb.
Water	54 lb.
Soap	1 lb.
Odorant	1 lb.

The odorant may be any essential oil and the soap should be a neutral organic one like glycol oleate, stearate, etc., or any of the ammonium salts of the fatty acids. These may also substitute for lanette wax in formula 2. Formula No. 1 can be compounded by simple mixing while Nos. 2 and 3 require more care in that the soap must be dispersed in the water, either hot or cold, depending upon the soap chosen, and the oils after mixing should be stirred into the cold soap solution with rapid agitation.

The nature of highly polished surfaces like metals, glass, wax, and varnish films has been examined by physico-optical methods (high-speed electrons and reflection diagrams) from which the conclusions were drawn that the degree of abrasion, plastic deformation in the surface, and leveling of the micelles in the surface were directly proportional to the speed and pressure of the polishing instrument. So, a furniture polish applied and subsequently buffed by hand can do little harm to a film, if no substances which exert a solvent effect are present. A. T. B.

Chemotherapy of malaria. S. P. JAMES. *Nature*, **136,** 743–5 (Nov. 9, 1935).—One paragraph in this article is rather amazing to the casual user of quinine. In a malaria district in Ceylon, about the size of Yorkshire, the cost of relief measures was about $1,750,000, and during the six months from November until April, fourteen and one-half tons of quinine, costing $250,000, was used. About $100,000 also was spent on a new anti-malarial remedy called "atebrin". In the note the author concludes that there is no absolute remedy for malaria at present, and that one of the most needed fields of research is in compounds which will aid in anti-malaria chemotherapy. F. B. D.

Dextrin manufacturing methods. J. A. RADLEY. *Chem. Industries*, **38,** 257–8 (Mar., 1936).—Manufacturing processes for dextrin fall into two broad classes: those in which the dry starch is heated alone, or with acid or acidic substances, and those in which a suspension of starch or a starch paste is treated with chemical agents or with enzymes. The first type of process yields dry-powder products varying in color from white through yellow to dark brown, while the processes of the second type give liquid products which are dried to coarse powders or pearl-shaped granules. A. T. B.

APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

A new volumetric determination of aluminum. W. DAUBNER. *Angew. Chem.*, **48,** 589 (Sept. 7, 1935).—A solution of the aluminum salt which is either neutral or faintly acid with acetic acid is treated with ammonium arsenate in the presence of ammonium chloride and acetic acid, with the precipitation of tertiary aluminum arsenate, $AlAsO_4$. The precipitated salt is filtered off and dissolved in hydrochloric acid, and the arsenic acid present is determined by titration. L. S.

A new sensitive method of detecting non-metallic impurities in metals. K. W. FRÖHLICH. *Angew. Chem.*, **48,** 624–7 (Sept. 28, 1935).—The presence of sulfides, arsenides, antimonides, phosphides, tellurides, and selenides in metals can be detected by changing them into the hydrides by the action of hydrogen formed on a cathode. These hydrides appear in the cathode gas and can be detected by means of suitable indicators and test papers. If the cathode material contains no more than 1% of metallic impurities it is possible to detect them quantitatively by comparison with cathodes of known metallic concentration. L. S.

A chemical hygrometer. T. M. CARPENTER. *J. Biol. Chem.*, **112,** 123–33 (Dec., 1935).—An apparatus for the determination of water vapor by volume in air is described. It is constructed on the principle of a gas-analysis apparatus in which the volumes before and after removal of water vapor by an absorbent are read against a constant volume kept dry by P_2O_5. A large number of comparisons with results obtained by weighing the water vapor absorbed from air containing 0.3 to 2.2% moisture show an agreement of under 0.02% on the average. The apparatus is portable and commercially easily produced. E. D. W.

A new unitized water bath. ANON. *Laboratory*, **7,** 54 (Jan., 1936).—As indicated by the term "unitized," the new bath is made up of individual, interchangeable units. The bath itself, a circular jar of heavy pyrex glass, permits full visibility of all immersed objects; all accessories are neatly tucked away to one side, leaving over 90% of the bath surface unobstructed, and the bath is very easy to keep clean. A low-lag electric immersion heater, with sensitive vapor thermostat control, permits quick and easy regulation of the temperature to 0.02°C. An efficient stirrer with plenty of torque insures complete circulation and uniform temperature.

The immersion heater consists of nichrome wire encased in copper coil. The thermostat is of the vapor sensitive type and operates a positive acting relay. A list of the sensitive liquids for bath temperatures up to 100°C. is given in a table. A. T. B.

A new contort clamp holder. ANON. *Laboratory*, **7,** 58 (Jan., 1936).—The new clamp holder consists of two holding members, set at a 90° angle, and connected by a double plate joint with precisely machined faces by which the different positions are held rigidly. Each member has freedom of movement in two directions, around its longitudinal axis and in a plane vertical to this axis. Two rods can thus be held at any angle to each other, from 0° to 180°. They can be made to touch or be swung away from each other as the need may be. A. T. B.

SCIENTIFIC REVIEWS AND BIBLIOGRAPHIES; TABULATIONS OF SCIENTIFIC DATA

The chemistry of the vitamins—II. K. H. COWARD. *Sch. Sci. Rev.*, **17**, 94–100 (Oct., 1935).—A review of vitamins C, D, and E, with 14 references. S. W.

The chemical elements and their discoverers. G. W. MUHLEMAN. *Laboratory*, **7**, 56–7 (Jan., 1936).—This two-page table, compiled by Prof. Muhleman, Hamline University, is very neatly arranged. It also includes the number of isotopes, the atomic numbers, the valence, the atomic weight, and the date of discovery. The table covers the center pages and could very conveniently be taken out of the book for posting in chemical laboratories or other places for teaching purposes. It is apparently up to date since it includes element 93, supposed to have been discovered by Fermi in 1934. A. T. B.

The noble metals. F. MICHEL. *Chem.-Ztg.*, **59**, 803–6 (Oct. 2, 1935).—A review of gold, silver, platinum, iridium, palladium, osmium, rhodium, and ruthenium. L. S.

The catalytic oxidation of ammonia-methane mixtures to hydrocyanic acid. L. ANDRUSSOW. *Angew. Chem.*, **48**, 593–5 (Sept. 14, 1935).—A review. L. S.

The formation, structure, and chemical utilization of amber. C. PLONAIT. *Angew. Chem.*, **38**, 605–7 (Sept. 21, 1935).—A survey. L. S.

PROFESSIONAL

The improvement of teaching in the college. J. T. ANDERSON. *J. Higher Educ.*, **7**, 36–41 (Jan., 1936).—Mr. Anderson, president of the State Teachers College of Nebraska, was chairman of the committee which guided a study of the literature on the improvement of college teaching. This study is summarized in these pages and hence does not lend itself readily to abstraction.

Mr. Anderson included in his summary the list of certain characteristics of successful college teaching which President Z. E. Scott, in an address before the American Association of Teachers Colleges during the February, 1935, meeting at Atlantic City, gave as representing the opinions of approximately forty men and women in colleges and universities, namely: "enthusiasm for, and broad scholarship in, one or more fields of knowledge"; "ability to deal with the principles in, and underlying, subject-matter, rather than mere facts within the subject-matter"; "an appreciation of what richness in learning means to the progress of civilization"; "open-mindedness toward all aspects of learning, toward life problems, and life attitudes"; "ability to arouse and stimulate the majority of students to self-activity along wholesome lines." A. T. B.

GENERAL

Speed versus control in chemical production. J. F. THOLL. *Chem. Industries*, **37**, 533 (Dec., 1935).—"One big, fundamental distinction separates the technic of the mechanical from that of the chemical industries. Speed, speed, more speed in every detail of each operation is the goal in the fabricating industries. In the process industries, on the other hand, control, continuous control, elegance of control, more accurate and more automatic control is the major objective." A. T. B.

Controlling the costs of industrial research. G. AMERMAN. *Chem. Industries*, **37**, 535–8 (Dec., 1935).—Concentration on the necessity for, and advantages of, scientific research work has almost blinded chemical management to the profit opportunities offered by business research and the scientific management methods so avidly installed by the mechanical industries. Chemical industry is thus in the unique position of being the leader in expenditures for scientific work and laggard in expenditures for methods research. Control of research on sound financial principles is as welcome to the sincere and thoughtful research executive as it is to the financial executive. A. T. B.

Glauber salt in North Dakota. I. LAVINE, H. FEINSTEIN, AND E. SKENE. *Chem. & Met. Eng.*, **42**, 681–2 (Dec., 1935).—An extensive field survey has been carried out during 1935 under supervision of the University of North Dakota as an employment project of the F.E.R.A. to investigate the sodium sulfate deposits of the state. The results of this survey, which are not entirely without promise, are summarized in this article. J. W. H.

American chemical industry marches on. ANON. *Chem. Industries*, **38**, 16–9 (Jan., 1936).—During the past year American chemical industries have made notable gains, measured by any one of several yardsticks.

Expenditures on the industries' capital account for plant and equipment may be estimated at about 60 million dollars, or half again as great as in 1934. The spread of activity is wider, since the total does not include anything comparable to the big plant expansions of the previous year by the three alkali companies.

Volume of trade (expressed in tons of chemicals shipped) has returned, so all agree, to the total of 1928. Several of the best informed sales departments estimate that 1935 tonnages are as much as 20 per cent. above that boom year's shipments.

Profits, as indicated by the earnings reports of the companies listed on the stock exchanges, are distinctly better than at any time since 1930. As a natural result, the value of chemical corporation shares has made rather sensational advances during 1935.

The past year has seen the commercial introduction of a number of promising new chemical specialties and the development of new chemical consuming processes, indicating that the industry is reaping the fruits of its well-sustained research programs.

While there has been but very small increase in the number of ordinary workmen employed in chemical works, nevertheless the reëmployment of trained technical men has been very great. There is no longer any acute emergency of unemployment among competently trained chemists and chemical engineers.

Looking forward, the year coming will see, barring unexpected political developments, a continuation of greater expansion in plants and equipment. Thirty chemical manufacturing companies, recently canvassed by *Chemical Industries*, report that during 1935 they have spent a total of $16,711,567 on new plants and equipment, and the same companies estimate that their expenditures in 1936 will be $22,076,000. A. T. B.

Safe chemical operations. P. J. CARLISLE. *Chem. Industries*, **38**, 48–9 (Jan., 1936).—P. J. Carlisle of the R and H Chemicals Dept. of du Pont, with headquarters at the Niagara Falls plant, outlined for the chemical engineers at the recent Columbus meeting the essential principles of safe operation in chemical manufacture. Safety is not a subject to be emphasized periodically by sporadic campaigns or other intermittent promotional plans. Only by the conscientious assumption of responsibility by the supervising chemist can valuable property and the health of employees be protected against the harmful effects of noxious materials.

In order to assure the attainment of safe operation, the supervising chemist must have the following knowledge.

1. A thorough knowledge of the characteristics of the raw materials being used.
2. A realization of the effect of such raw materials, alone or in combination, upon the health of the persons involved in the work, upon the property involved, and upon the continuity of operation.
3. A thorough knowledge of and acquaintance with the available equipment which can be used to protect life and property against the possible ill effects of raw material.
4. A knowledge of the preferred operating procedure to be followed in using such raw material. A. T. B.

British chemical gains. L. W. JONES AND N. W. VERE JONES. *Chem. Industries*, **38**, 19–22 (Jan., 1936).—Distinct improvement in trade, which set in during the latter half of 1934, continued during the early months of 1935. There has been evidence of some hesitancy during later months, and advances have been consolidated rather than extended. Great Britain in comparison with the rest of the world has more than held her position.

Within the recovery, chemicals hold their position and production has been maintained remarkably constant at the high level reached in the last quarter of 1934. Export and import figures for the first 10 months, taken from the Board of Trade returns, are given. A. T. B.

RECENT BOOKS

THE IDEAS OF PHYSICAL CHEMISTRY. *H. McKay*, B.Sc., and *H. A. C. McKay*, Gibbs Scholar in Chemistry, Oxford University. William Heinemann, Ltd., 99 Great Russell Street, London, W.C. 1, 1934. Chemical Publishing Co., 175 Fifth Ave., New York City, exclusive agents in North and South America. x + 301 pp. 87 figs. 14 × 21 cm. $4.00.

The authors have not included a preface to their book so that the reviewer is forced to gain whatever information he can as to their purpose from what has been printed by the publisher on the paper outer cover. Here it may be inferred that the book is addressed to the layman or to the non-chemical specialist and is intended as a non-mathematical introduction to the subject of physical chemistry. If this be the authors' purpose, they have succeeded admirably in certain chapters but have forgotten their prospective readers entirely in others. The reader is told, for example, on p. 181 that "Ag is the symbol for silver"; but on p. 175 he is faced with "If E is the energy of activation, a fraction $e^{-E/RT}$ of the collisions lead to reaction. Here e is the exponential function, 2.718, R is the gas constant, and T is the absolute temperature." The impression left with the reviewer, after a careful study of its chapters, is that the book is of a curiously uneven quality. Each chapter considered by itself has indubitable merit and could be read with profit by readers at a certain stage in their scientific education. However, the ease with which the subject matter can be understood varies to such an extent from chapter to chapter that it seems doubtful if the entire book can be recommended to any one class of readers.

The following general topics are treated: the ultimate particles, isotopes, transmutation, the Bohr theory, the periodic table, chemical links, giant molecules, wave mechanics, polar molecules, solutions, molecular spectra, crystals, X-rays and chemistry, stereochemistry, molecular structure, reaction velocity, photochemistry, chain reactions, adsorption and catalysis, corrosion, surface films, the Brønsted definition of acids and bases, conductivity and the Debye-Hückel theory, transport numbers, colloids, and a survey of physical chemistry. A vocabulary of chemical terms and a short bibliography are included.

A serious omission is that of any discussion of thermodynamics, surely one of the fundamental ideas of physical chemistry. For the most part theories are presented with little attempt to explain their derivation from the basic experimental facts. These facts are mentioned in many instances but how the postulates of the theory may be inferred from them is too frequently left unexplained. The reviewer realizes that anything approaching a quantitative explanation would involve a mathematical treatment far beyond the ability of the readers to whom the book is addressed. However, a qualitative explanation would have been possible in many instances where none has been given.

JOHN A. TIMM

YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

PROBABILITY AND RANDOM ERRORS. *W. N. Bond*, M.A., D.Sc., F. Inst. P., Lecturer in Physics, University of Reading. Edward Arnold & Co., London, 1935; Longmans, Green and Company, New York City. viii + 141 pp. 16 figs. 13.5 × 22 cm. $3.75.

In this book, intended for use by physicists and chemists, the author has "endeavored to avoid advanced mathematical methods, but to discuss fundamental assumptions in detail." The first two chapters deal with elementary problems in probability and introduce the reader to the type of reasoning which underlies the treatment of the more complicated problems of the following seven chapters. The content of the latter may be judged from their titles: III—Types of Error; IV—Estimation of Errors; V—The Combination of Observations; VI—Linear Graphs and Correlation; VII—Curve Fitting; VIII—Periodic Curves; IX—Miscellaneous Examples.

These are followed by Appendix I, containing a summary of the chief formulas, and Appendix II, giving a special treatment of the case where only two observations are made.

In general the author has avoided any discussion of the derivations of the formulas, but has emphasized their applicability and application to the evaluation of such data as are commonly obtained by physicists and chemists. Many numerical examples are worked out where the estimated values and errors may be compared with actual values and errors. The assumptions underlying the various methods of evaluations are discussed, and comparisons of the methods made in many problems.

This book should prove to be of particular value to chemists who wish to treat their results by statistical methods but whose lack of mathematical background has discouraged them from attempting to do so.

PAUL C. CROSS

STANFORD UNIVERSITY
CALIFORNIA

NOTES ON ORGANIC CHEMISTRY. *F. Francis*, Alfred Capper Pass Professor of Chemistry, University of Bristol. Longmans, Green and Company, New York City; Edward Arnold and Company, London, 1935. viii + 525 pp. 14.5 × 23 cm. $4.00.

This book is accurately described by its title. It is a collection of notes such as might be made by an organic chemist as he reads the literature. They are arranged in chapters on various topics. This method is a departure from the usual fashions of scientific writing.

The experiment is in part successful. One can open the book at random and find interesting and valuable information. But in publishing a set of notes on so varied a subject as organic chemistry, the author is on the horns of a dilemma. Either he restricts the number of topics so much that organic chemistry does not describe the contents, or he restricts the notes on each topic so much that the specialist finds them inadequate. On the whole the author chooses the latter alternative, though many important subjects, *e. g.*, the free radicals, are omitted.

Although the book is in no sense a textbook, it should have its greatest appeal to university students. To them it should be an appetizer for further knowledge of organic chemistry. It would seem that the author had such a use in mind, for blank pages have been left for the reader to fill with his own notes.

A greater number of references to the original literature would have increased the usefulness of the book, but would have detracted from its pleasing informality.

GERALD BRANCH

UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.

A COURSE OF PRACTICAL ORGANIC CHEMISTRY. *T. S. Price and D. F. Twiss.* Fourth edition. Longmans, Green and Co., London, 1935. xiii + 238 pp. 35 figures. 14 × 21.6 cm. $2.75.

This British laboratory manual was originally designed "to provide a course of work in Organic Chemistry for evening students attending Technical Institutions with a view to working for the examinations of the Board of Education or for the B.Sc. degree." Prefaces to later editions indicate that the book has found "increased use in various University and Technical College laboratories," by both day and evening students, but that the general character of the first edition has been retained throughout the several revisions. The manual is intended "as an introduction to the methods of practical organic chemistry," and not for "students who are taking more advanced and detailed courses."

The book contains more than ample material for almost any undergraduate course. It presents examples of the processes generally considered appropriate to elementary courses. The choice of experiments is conventional. The scope and variety of exercises permits (or requires) a selection to be made.

The first chapter describes the determinations of melting point, boiling point, and specific gravity and the tests for elements, and gives suggestions for the purification, etc., of organic preparations. With exceptions noted below the succeeding chapters are devoted to experimental procedures for preparations and tests, with brief explanatory sections. The arrangement of the experiments is far from systematic, though to some extent logical. As an example Chapter II ("Monobasic Acids, Etc.") contains the following: preparation of stearic acid from suet; a series of preparations from acetic acid, *viz.*, monochloroacetic acid, acetamide, acetonitrile, methylamine hydrochloride; preparation of oxalic acid from cane sugar; tests for oxalic acid (5 tests), tartaric acid (8), citric acid (5), and succinic acid (4); preparation of diethyl oxalate, dimethyl oxalate, and oxamide; preparation of formic acid and of allyl alcohol from oxalic acid and glycerol; 5 tests on glycerol; preparation of urea by Wöhler's method, and 6 tests on urea; preparation of semicarbazide, recovered as acetone semicarbazone. In view of the diversity of experiments in some of the chapters, the basis for the division of the book into chapters is at several points rather obscure. In the reviewer's opinion there are too many test-tube or equivalent reactions for individual compounds. Some instances were mentioned above, and there are many others throughout the book; *e. g.*, for cyanides (6 tests), ferrocyanides (7), ferricyanides (6), benzoic acid (7), salicylic acid (8), benzaldehyde (4). Chapter XVI is devoted entirely to descriptions of, and tests (58 in all) on, fourteen heterocyclic compounds, mostly alkaloids.

There are two chapters on the identification of organic compounds, one following the aliphatic section and the other at the end of the text. The schemes presented are designed primarily for identification of the compounds studied in the laboratory course. This permits the use of procedures much less rigorous than would be required for a more extensive list of compounds. Identifications are completed by physical constants, special tests, etc., but seldom by preparation of derivatives.

A chapter is devoted to the quantitative analysis of organic compounds for carbon, hydrogen, nitrogen, halogens, sulfur, and phosphorus (the last two are only outlined), mostly by classical methods. This section is only passably satisfactory. In the determination of carbon and hydrogen, water is absorbed in sulfuric acid in a U-tube, and carbon dioxide in potassium hydroxide solution in a potash bulb; no mention is made of a blank run. In the Dumas method no blank is run on the tube-filling. In the Kjeldahl method a short-necked flask is used for digestion and distillation. The digestion is made without the aid of a catalyst, the accelerating action of copper sulfate (or potassium chlorate) being mentioned in a footnote. No blank is run on the reagents.

The chapter on the determination of molecular weights describes the commoner chemical and physical methods in adequate fashion. The micro-method of Rast is omitted.

There is another chapter on quantitative methods, including saponification procedures for esters, nitriles, and amides, and the Zeissel method using the Perkin apparatus. Following is the chapter on tests with heterocyclic compounds, and then the qualitative analytical scheme, both mentioned above. There is a brief appendix giving some tables of constants and the compositions of some reagents.

Directions are plainly given, and the procedures generally satisfactory, though a few exceptions may be noted. There is included the old aldehyde-ammonia experiment, now wisely omitted from many laboratory manuals as wasteful of time and chemicals, and not compensatingly instructive. In the "Preparation of Pure Alcohol from Methylated Spirit, or Spirits of Wine," the distillation from a tin can and without a column is not likely to yield from "methylated spirit" a specimen of ethanol whose purity can be judged from its specific gravity. Quinoline is prepared by the old method, which occasionally gets out of control. The course of the Skraup reaction given is not the one now generally accepted. Among instructive experiments which are omitted may be mentioned the furfural reaction of pentoses and the Hinsberg separation of amines. Some relatively unimportant tests, for example the formation of hydrocarbon picrates, appear more than once.

Melting- and boiling-points (rounded off to whole numbers) are in some cases not the best values. Literature references are given sparingly, and with one exception to papers in British journals. In a number of cases preparations are made on a scale which seems unduly large. Some references to industrial processes do not represent current practice, at least not for this country.

E. C. WAGNER

UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNA.

A SHORT ORGANIC CHEMISTRY. *F. Sherwood Taylor*, Assistant Lecturer, East London College. William Heinemann, Ltd., London, 1933. Chemical Publishing Co. of N. Y., Inc., exclusive American agents for this book. viii + 378 pp. 13.5 × 21.5 cm. 43 figs. $3.00.

The author informs us that this is a shorter version of his "Organic Chemistry" and feels that "this book contains all that is likely to be of use to the first-year student of the subject." For one term the material is enough, but it would hardly suffice for a full year.

The treatment is of the usual type with no glaring novelties. Electronic formulas are used in the few places in which they are useful but are not featured. In the interest of completeness many classes of organic compounds are described, but for brevity only the lower members, usually two or three, of a series are mentioned. Olefins are introduced later than in many texts. Aromatics take up slightly over one-third of the space.

Fifty-three laboratory experiments with figures and satisfactorily full directions are included, so that the book is a combined text and laboratory manual. There are a number of full-page diagrams, in each of which an important compound occupies the center and is surrounded by the compounds which may be made from it, with indications of the methods used.

The information given is usually as correct as can be given in a changing world. American students will be interested to know that industrial alcohol is made from potatoes. Certain American manufacturers will be surprised to learn that isopropyl alcohol "is usually prepared by reducing acetone with sodium amalgam and water."

On the whole the book is well done and gives the student a well coördinated view of organic chemistry.

E. EMMET REID

THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

SULFURIC ACID MANUFACTURE. *Andrew M. Fairlie*, Consulting Chemical Engineer; Consultant for American Zinc Oxide Co., Tennessee Corporation, The Farmers Fertilizer Co., etc. American Chemical Society Monograph No. 69. Reinhold Publishing Corporation, New York City, 1936. xxii + 646 pp. 187 figs. 98 tables in text and appendices. 15.3 × 22.5 cm. $9.75.

In this monograph, according to the author, "The attempt has been made here to produce a book on sulfuric acid manufacture which would be of practical use to the chemical engineer, the technical chemist, the acid manufacturer (actual or potential), the student at college or technical school, and the acid consumer, without clogging the text with lengthy descriptions of obsolete processes, or of mere proposals that have not been reduced to practice. In order to keep within the limits of a single volume, pertinent matter already available elsewhere has been omitted, and the temptation to expand the treatment of various topics has been resisted; but in all cases copious references have been introduced to supply the reader with information as to sources where the omitted matter may be found." American practice has been featured, but foreign developments have been briefly described and references for further study are given.

The introduction deals with the properties of sulfuric acid; the nomenclature used in the industry; the uses of sulfuric acid; and statistics of its manufacture. The history of sulfuric acid is briefly discussed in Chapter 1. Following this are chapters

on: the chemistry and theory related to sulfuric acid manufacture; construction materials; production materials; the burners, roasters, and furnaces used to produce sulfur dioxide from brimstone, pyrites, zinc ore, copper ores, and copper matte; burner or furnace gas, its composition and a general discussion of its purification.

The exposition of the nitration processes requires about one-third of the book. The ammonia oxidation method of nitration is described in detail and little space is given to the older sodium nitrate method which, the author states, "may be considered obsolete." Separate chapters are given to: the Glover tower, lead chambers, Gay-Lussac tower, and auxiliary equipment. Such details as design, size, temperature control, and operation are discussed. In the chapter on lead chambers considerable space is given to special types of lead chambers and the tower systems which have been designed to supplement or replace lead chambers. A chapter is devoted to a discussion of a complete plant, its layout, starting into operation, operation, control, shutting down, maintenance, and yields. Under purification, the author deals with: effects of the various impurities upon plant equipment and operation, and upon the uses of the product; the avoidance or the elimination of these impurities; and the recovery of sludge and waste acid in various industries. A discussion is given of the theory and the various modern equipment used to concentrate dilute acid.

Slightly more space is given to the contact or catalytic processes than to the nitration processes, even though about 60 per cent. of all sulfuric acid is made by the latter processes. The author gives statistics to show that the amount of sulfuric acid made by the contact processes is increasing. The topics treated are: a general discussion of the steps involved; detailed discussion of the principles involved in each step and the types of apparatus used; the catalysts used; the layout of a complete contact plant, its operation and control; and the special types or adaptations of contact plants. Considerable attention is paid to the methods of purification and the control of the temperature of the burner gas. A general description is furnished of the preparation of the various catalyst masses, the amounts needed, the method of determining the activity, and the regeneration of platinum masses. There is a short account of the legal controversies regarding the vanadium oxide catalysts. A detailed comparison of the various platinum and vanadium catalysts gives the merits and disadvantages of each.

The last chapter contains miscellaneous information on: mixing and shipping of sulfuric acid; hazards and safety measures; costs and cost accounting; factors to be considered when a user of sulfuric acid is faced with the problem of buying acid or building a sulfuric acid plant; and trends in the industry.

The 15 appendices contain tabulated information of practical value to the chemical engineer and acid manufacturer such as hydrometers, sulfuric acid tables, sulfuric acid temperature conversion tables, brick shapes, nomographs for finding specific volumes of sulfuric solution, etc.

The book is an indispensable reference for those who are making a study of any phase of American sulfuric acid manufacture. The author has used his wealth of plant and consulting experience to present a clearly written practical treatise with a minimum of technicalities. The numerous references to the literature are a valuable aid to those who need to study in detail some phase of sulfuric acid manufacture.

RUFUS D. REED

NEW JERSEY STATE TEACHERS COLLEGE
UPPER MONTCLAIR, NEW JERSEY

CHEMISTRY WORKBOOK AND LABORATORY MANUAL. *Russell S. Howard*, Lyons Township High School and Junior College, La Grange, Illinois. Henry Holt and Company, New York City, 1936. xi + 306 pp. 65 figs. 19.7 × 28 cm., detachable, punched. $0.96.

This book is primarily a laboratory manual designed to accompany the author's "Units in Chemistry." The workbook, viewed as a set of drill exercises, is not included. The experiments are grouped about eight major units, each unit being illustrated by from four to twelve experiments. Each numbered experiment is in turn divided into several independent experiments, each followed by related questions. The instructor is thus furnished with a wide choice of material.

The form of pupil reporting of the experiments is unique. The significant observations are brought forth by questions which require brief answers. Deductions from these observations are followed immediately by other questions, which are likewise to be answered briefly. Opportunity for originality in observations is limited, the irrelevant avoided, and opportunity for inductive thought is increased by the sharp focus.

Many experiments not ordinarily performed in the introductory chemistry course are included. The use of common substances—butter, putty, clay, coal, iodized salt—adds interest. The phenomena of rain and of swelling due to insect bites are reproduced in a test-tube. The experiments on colloids are well chosen. Many satisfactory quantitative experiments are included. Helpful information on solution concentration is given handily.

The book is well done, quite free from errors (although one wonders why a hydrogen generator should be heated, Fig. 21), and is recommended where a strong laboratory course is desired. The author has exemplified his philosophy of the "LABORatory, not labORATORY," set forth in one of the preliminary discussions, "The laboratory is not an appendage hung on the chemistry recitation room."

ELBERT C. WEAVER

BULKELEY HIGH SCHOOL
HARTFORD, CONN.

PRACTICAL PHYSICAL CHEMISTRY. *Alexander Findlay*, Professor of Chemistry, University of Aberdeen. Sixth edition. Longmans, Green and Co., New York City, 1935. xii + 318 pp. 117 figs. 13.8 × 21.5 cm. $2.50.

The latest edition of this book is the result of a general revision and the introduction of several new subjects. The added items include the use of vacuum tubes in the regulation of thermostats; the specific gravity balance; the torsion balance for surface tension measurement; use of oscillators and other alternating current sources in conductivity determinations; use of the carborundum detector in analysis by conductance; the glass electrode; determination of transport numbers from electromotive force measurements; adsorption and catalysis.

As in the previous editions, the first two chapters are devoted to a discussion of errors and chemical technic, while the third chapter gives a review of thermostats and regulating devices for thermostats. The other chapters give short discussions of the theory and descriptions of experiments on density of gases and liquids, viscosity, surface tension, optical measurements, osmotic properties of solutions, distribution between two non-miscible solvents, conductivity of electrolytes, transport numbers, electromotive force measurements, velocity of chemical reactions, thermochemistry, heterogeneous equilibrium, and colloids.

In order to keep abreast of the developments in science, this book, one of the standard laboratory manuals in physical chemistry, has gone through frequent revisions. The reviewer's experience has proved that the experiments are workable and the directions clearly given. The descriptive material forms a good supplement to classwork and gives the student an insight into laboratory technic.

Some minor additions to what is a very good book on experimental physical chemistry might be made by expanding the sections on homogeneous equilibria, colloids, and sources of alternating current, and adding experiments on boiling point-vapor composition curves and modern theories of acids.

The teacher can certainly find sufficient experiments for the laboratory work of a one-year course in physical chemistry and the student gains much valuable information concerning physical-chemical apparatus. The book is recommended for these purposes.

ARTHUR A. VERNON

RHODE ISLAND STATE COLLEGE
KINGSTON, RHODE ISLAND